PB89-224786

Reduction of Arsenic Wastes in the Electronics Industry (Application to Study)

Envirosphere Co., Santa Ana, CA

Prepared for:

California Dept. of Health Services, Sacramento

Jun 87

U.S. Department of Commerce
National Technical Information Service
NTIS

PB89-224786

FINAL REPORT

STATE OF CALIFORNIA

DEPARTMENT OF HEALTH SERVICES
TOXIC SUBSTANCES CONTROL DIVISION
ALTERNATIVE TECHNOLOGY AND
POLICY DEVELOPMENT SECTION

Application To Study The Reduction Of Arsenic Wastes In The Electronics Industry AB685 Grant Program

Grant Number
85-00178

JUNE 1987

Envirosphere Company

in cooperation with

Hewlett-Packard Company

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL INFORMATION SERVICE
SPRINGFIELD, VA. 22161

50272-101

REPORT DOCUMENTATION PAGE	1. REPORT NO. 005-015 A	2.	3. Recipient's Accession No. PB89 224786/AS
4. Title and Subtitle: The Reduction of Arsenic Wastes in the Electronics Industry: Final Report			5. Report Date: June 1987
			6.
7. Author(s)			8. Performing Organization Rept. No.
9. Performing Organization Name and Address: Envirosphere Company, 3000 W. MacArthur Blvd., Santa Ana, CA 92704			10. Project/Task/Work Unit No.
			11. Contract(C) or Grant(G) No. (C) (G) 85-00178
12. Sponsoring Organization Name and Address: California Department of Health Services, Toxic Substances Control Division, Alternative Technology Section, 714/744 P Street, Sacramento, CA 95814			13. Type of Report & Period Covered
			14.

15. Supplementary Notes
This document is included in the Pollution Prevention Information Clearinghouse, operated by Science Applications International Corporation (SAIC), for the U.S.EPA, at 8400 Westpark Drive, McLean, Virginia 22102.

16. Abstract (Limit: 200 words)

This publication is the final report of a group studying the reduction of arsenic wastes in the electronics industry. They used the gallium arsenide (GaAs) chip manufacturing process at the Hewlett-Packard Company's San Jose facility as a model. The study found that ingot grinding and slicing produced approximately 90% of all arsenic waste. They also discovered that 95% of arsenic waste existed in the particulate form. These findings indicated that a filter in combination with a filter press could recover the vast majority of arsenic from the wastewater stream. In addition to recovering a valuable product (GaAs), the arsenic waste currently transported as an extremely hazardous waste to a class I landfill, would be reduced by greater than 95%.

17. Document Analysis a. Descriptors

pollution prevention, recovery

b. Identifiers/Open-Ended Terms

c. COSATI Field/Group

18. Availability Statement	19. Security Class (This Report)	21. No. of Pages
Release unlimited		115
	20. Security Class (This Page)	22. Price

(See ANSI-Z39.18) See Instructions on Reverse

OPTIONAL FORM 272 (4-77)
(Formerly NTIS-35)
Department of Commerce

envirosphere company
A Division of EBASCO SERVICES INCORPORATED
3000 W MacArthur Blvd., Santa Ana, CA 92704 (714) 662-4050

June 30, 1987

Mr. Frank Mele
Department of Health Services
Toxic Substances Control Division
Alternative Technology and Policy
Development Section
714/744 P Street
Sacramento, CA 95814

SUBJECT: FINAL REPORT FOR GRANT NUMBER 85-00178:
THE REDUCTION OF ARSENIC WASTES IN THE
ELECTRONICS INDUSTRY

Dear Mr. Mele:

Envirosphere Company in cooperation with Hewlett-Packard Company is pleased to submit eight (8) copies of our final report for the study of arsenic waste reduction in the electronics industry. This project has represented a unique study opportunity because Hewlett-Packard Company has made available for investigation a full-scale manufacturing process. Ms. Gail Brownell, Project Director and Facility Environmental Engineer, Hewlett-Packard Company, San Jose, California, acted as official liason with various manufacturing personnel so that each process step producing arsenic could be tested. In many cases, Hewlett-Packard personnel interrupted their normal work process to accommodate the conduct of our project.

The Project Staff wish to acknowledge the positive direction and management under your charge that we have received from the Department's Alternative Technolgy and Policy Development Section.

Implementation of the findings of our study will allow for the following:

- Recycling of gallium arsenide
- Substantial elimination of arsenic transport to a hazardous waste landfill

In conclusion, we feel that Envirosphere, Hewlett-Packard, and the Department have worked well together. We look forward to working together again for the Step II Application and for our Step I Solvent Reduction Application.

Sincerely,

Richard L. Jenkins

Richard L. Jenkins, Ph.D, P.E.
Project Manager

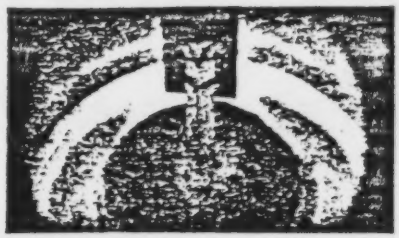
RLJ/mjo

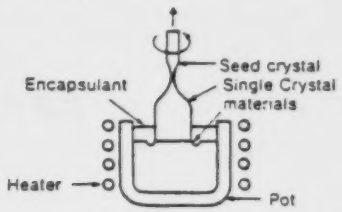
j.b

SELECTED GALLIUM ARSENIDE CHIP MANUFACTURING PROCESS STEPS

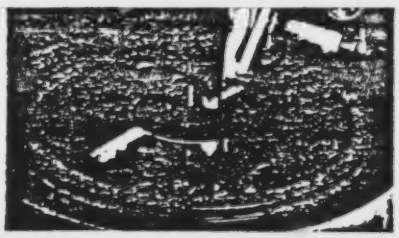
CRYSTAL–WAFER PROCESS

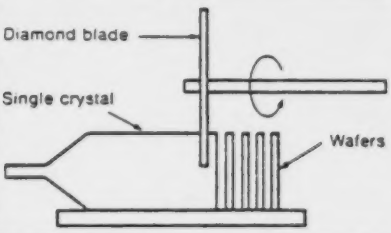
Crystal Growth *1*



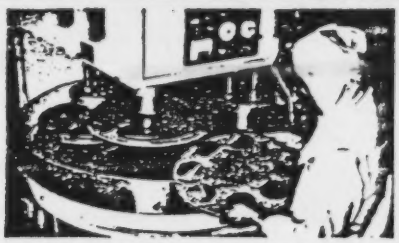


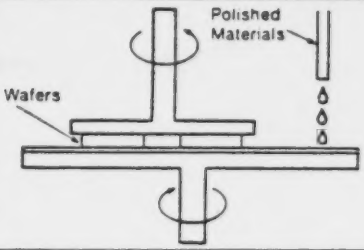
Wafer Slicing *2*





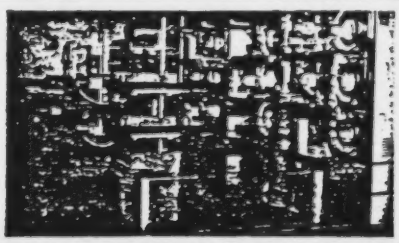
Wafer Polishing *3*

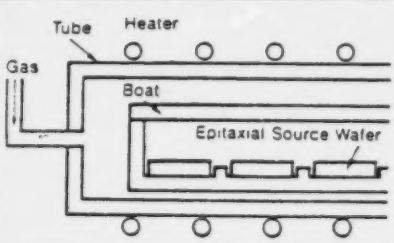




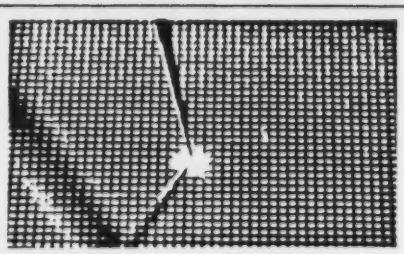
EPITAXIAL–CHIP PROCESS

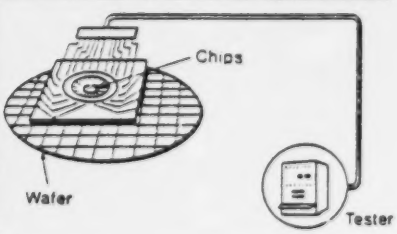
Liquid Phase Epitaxial *1*



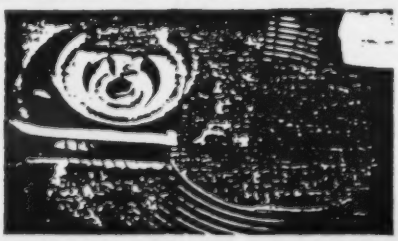


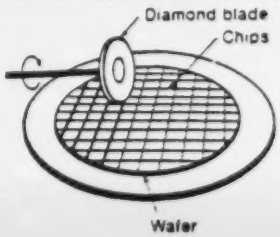
Electrical Testing *2*





Chip Dicing *3*





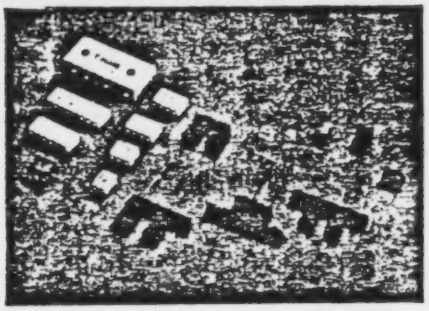
Reproduced from best available copy.

i.c

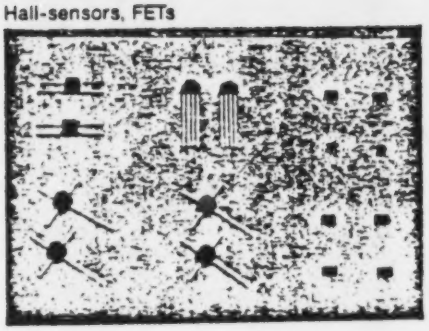
EXAMPLES OF GaAs PRODUCTS

GaAs Materials

Photo-sensors, Photo-couplers



Hall-sensors, FETs



PROJECT ABSTRACT

The gallium arsenide (GaAs) chip manufacturing process at Hewlett-Packard Company's San Jose Facility was used as a model to study the reduction of arsenic waste in the electronics industry. Although arsenic is produced from some 11 (eleven) different manufacturing steps, ingot grinding and slicing produced approximately 90% of all arsenic waste. For all arsenic waste produced, greater than 95% was found to exist in the particulate form. The findings of this study indicate that a filter in combination with a filter press could recover the vast majority of arsenic from the wastewater stream. In addition to the benefit of recovering a valuable product (GaAs), the arsenic waste which is currently transported as an extremely hazardous waste to a Class I landfill would be reduced by greater than 95%.

ACKNOWLEDEGMENTS

The Project Team thanks Alan Clark, Production Engineer, for his efforts in providing data on the amounts of waste gallium arsenide generated during ingot processing. Without Mr. Clark's assistance, our project schedule would have been seriously protracted.

We also want to thank the Hewlett-Packard Manufacturing staff in general for their cooperation.

DISCLAIMER

The statements and conclusions of this report are those of the Grantee and not necessarily those of the State of California. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

TABLE OF CONTENTS

	PAGE
SUMMARY AND CONCLUSIONS	viii
RECOMMENDATIONS	ix
1.0 INTRODUCTION	1
2.0 RESULTS AND DISCUSSION	3
2.1 GALLIUM-ARSENIDE MICROCHIP MANUFACTURING PROCESS	3
2.2 CHEMICAL CHARACTERIZATION OF WASTE STREAMS	7
2.3 ARSENIC CHEMISTRY	16
2.3.1 Elemental Arsenic	16
2.3.2 Compounds of Arsenic	18
2.3.3 Physical - Chemical Aspects	21
2.3.4 Environmental Cycling of Arsenic	23
2.3.5 Health Effects of Arsenic and Compounds	24
2.4 IDENTIFICATION OF POTENTIAL TREATMENT PROCESSES	30
2.4.1 Introduction	30
2.4.2 General Discussion	30
2.4.3 Filtration	36
2.4.4 Precipitation with Sodium Sulfide	45
2.4.5 Solidification	54
2.4.6 Ion Exchange	58
2.4.7 Adsorption by Activated Carbon	61
2.4.8 Adsorption by Activated Alumina, Bauxite and Carbon	65
2.4.9 Arsine Generation	68

TABLE OF CONTENTS

	PAGE
2.5 EVALUATION OF THE RECOMMENDED TREATMENT PROCESS-FILTRATION	69
2.6 ENVIRONMENTAL PERSPECTIVE	74
2.6.1 Reduction of Volumes of Arsenic Waste Generated Statewide	79
2.6.2 Acceptability by Industry	79
2.6.3 Transferability to Other Industries	79

REFERENCES

LIST OF INVENTIONS REPORTED AND PUBLICATIONS

GLOSSARY OF TERMS, ABBREVIATIONS, AND SYMBOLS

APPENDIX A - APPLICATIONS TO STUDY THE REDUCTION OR ARSENIC WASTES IN THE ELECTRONICS INDUSTRY - AB685 GRANT PROGRAM CONTRACT DOCUMENT

APPENDIX B - STATE OF CALIFORNIA ENVIRONMENTAL AND HEALTH AND SAFETY REGULATIONS

LIST OF TABLES

2.2-1 Recommended Data and Sample Acquisition - Hewlett-Packard

2.2-2 Arsenic Process Wastewater Data Summary

2.3-1 Trends in Properties of Elements of the Nitrogen Family

2.3-2 Toxic Effects of Arsenic

2.4-1 Summary of Arsenic Treatment Methods and Removals Achieved

2.4-2 Treatment Systems for Arsenic Removal

2.4-3 Pilot Plant Arsenic Removal

2.4-4 Arsenic III - Sulfide Precipitation Reactions

2.4-5 Analysis of Actual Scrubber Blowdown Waters

2.4-6 Effect of Iron/Arsenic Ratio on Arsenic and Heavy Metal Separation

2.4-7 Analysis of Inlet Wastewater (Full Scale Plant)

2.4-8 Removal of Metals by Sulfide Precipitation and by Sulfide Precipitation Followed by Lime Precipitation (Full Scale Plant)

2.4-9 Comparison of Adsorption Capacity by Various Types of Powdered Activated Carbons

2.4-10 Comparison of Adsorption Capacity by Various Type of Granular Activated Carbon

2.5-1 Comparison of Potential Arsenic Treatment Processes

LIST OF FIGURES

2.1-1 Sealed Quartz Ampoule GaAs Growth System
2.1-2 Liquid Encapsulated Czochralski (LEC Cz) Ingot Growth System 174
2.1-3 Gallium-Arsenide Ingot Crystals
2.1-4 Gallium-Arsenide Ingots and Wafers

2.2-1 Arsenic Wastewater Flow Diagram
2.2-2 Arsenic Production Rates
2.2-3 Percent Arsenic to HF Treatment System and Recycled Solids
2.2-4 Daily Liquid Flowrates

2.3-1 The Generalized Geochemical Cycles for Arsenic

2.4-1 Waste Reduction Components
2.4-2 Mechanisms of Filtration
2.4-3 Beta Values in Use
2.4-4 Filtration Equipment
2.4-5 Selection of Separation Process by Particle Size and Contamination Level
2.4.6 Sulfide Precipitation Plant (Boliden Metall, Sweden)
2.4.7 Effect of Ratio of Fe/As on Arsenic Removal by a Combination Hydroxide - Sulfide Precipitation

2.5-1 Selection of Separation Process by Particle Size and Contamination Level

2.6-1 Waste and Unit Classifications Used in California
2.6-2 Relationship Between Waste Classifications and Concentrations of Toxic Constituents

SUMMARY AND CONCLUSIONS

1. Arsenic contamination of the HF Treatment process results almost entirely from overflow of the Gallium Arsenide (GaAs) Slurry Recovery process liquid.

2. The sludge cake recovered from the HF Treatment System filter press is classified currently as Extremely Hazardous by Title 22 Section 66699 of the California Administration Code due only to its arsenic content.

3. An arsenic content reduction of 50 percent or greater in the overflow fluid from the GaAs Slurry Recovery system to the HF Treatment system will allow the sludge cake product to be reclassified as hazardous due only to its fluoride content.

4. Results of the Waste Extraction Test on the sludge cake material indicate arsenic is in an extremely inert and non-leachable form.

5. Hewlett-Packard's Gallium - Arsenide process is composed of many batch and semi-batch processes. The entire GaAs production system also can be considered a semi-batch process.

6. Waste reduction technology for removal of suspended arsenic solids from liquid streams appears to be easily transferable to other industries where heavy metal solids are involved.

7. Effective implementation of slurry recovery process filtration not only will eliminate arsenic-related hazardous wastes at Hewlett-Packard, but will increase the recyclable GaAs solids for sale to a recycle manufacturer.

9. The elimination of arsenic related hazardous wastes at Hewlett-Packard's San Jose facility will not require modifications of any of the steps currently necessary for GaAs microchip production.

10. The predominant form of arsenic in the GaAs microchip manufacturing process waste is particulate GaAs.

RECOMMENDATIONS

1. Filtration of all liquids entering the Gallium Arsenide (GaAs) Slurry Recovery process is recommended as the most cost effective and simple hazardous waste reduction technology investigated.

2. Further engineering studies, specifications, and design are recommended prior to installation of any filtration system.

3. Hewlett-Packard Corporate policy states that any process considered for arsenic waste reduction must make employee health and safety the paramount design criteria. Filtration systems available today routinely meet these design criteria.

1.0 INTRODUCTION

Many electronic companies in the State of California process or manufacture gallium arsenide (GaAs) microchips, which creates a substantial volume of waste containing arsenic. Generally, the concentration of arsenic in wastewaters or sludges exceeds sewer and municipal landfill limits for disposal, which usually requires these waters to be treated and disposed to a Class I hazardous landfill. This practice is not only expensive, but undesirable environmentally and economically as a long term mechanism for waste disposal.

This project has reviewed various processes to reduce, recycle and/or treat arsenic-laden wastes in a manner such that costs and disposal to the land are significantly reduced. The methods evaluated at various manufacturing stages included, but were not limited to, separation, precipitation/ fixation, ion exchange, and arsine generation.

The information from this study is suitable for 1) design of a pilot or full scale treatment facility; and 2) widespread use within the electronics industry. Since the electronics industry is so large in California, particularly in Silicon Valley, the technological advances from this study should form the basis for other electronic businesses and facilities to reduce arsenic waste disposal to the land. Further, the treatment processes recommended by this study may be applicable to other industrial waste disposal problems involving arsenic.

The Hewlett-Packard Company (HP) currently operates a gallium arsenide (GaAs) microelectronics chip manufacturing facility in San Jose, California. In the manufacturing process a solution of hydrofluoric acid is produced which contains significant levels of arsenic as well as non-hazardous constituents. The hydrofluoric acid solution is currently neutralized with lime which yields a calcium fluoride sludge containing high levels of arsenic. Other electronics companies utilize little or no treatment and haul the entire waste volume to a treatment storage and

disposal facility (tsdf). In 1985, HP produced 887,500 gallons of hydrofluoric acid wastewater and 25,219 gallons of calcium fluoride sludge.

The objective of this project was to investigate processes to reduce substantially the amount of arsenic which Hewlett-Packard must dispose to the land. The results of this study have led to a proposed process to recycle or reclaim the arsenic from the wastes, hence eliminating land disposal of arsenic.

2.0 RESULTS AND DISCUSSION

2.1 DESCRIPTION OF GALLIUM ARSENIDE MICROCHIP MANUFACTURING PROCESS[33]

The various manufacturing process steps which are described in the following pages are currently or potentially could be conducted at the Hewlett-Packard facility in San Jose.

Microelectronics is a revolutionary technology which has expanded enormously in the last two decades, becoming of major economic and technological importance to the world. The development of semiconductor devices, first germanium and then silicon diodes, followed by the transistor and the integrated circuit, were the major factors in the evolution of micro-electronics. The use of gallium-arsenide compounds have also greatly contributed to the advancement of modern electronics.

The principal focus in recent years on a silicon alternative has concentrated on valence III/V compounds, such as gallium arsenide (GaAs), as a substrate material. As a semiconductor material, GaAs exhibits increased capabilities over silicon, such as electron mobility five to six times that of silicon. This characteristic, coupled with the semi-insulating substrate of GaAs, leads to increased performance in both speed and power consumption.

The technology involved in the growth of GaAs crystals is considerably more complicated than that employed for silicon, and requires more precise control in the ingot growth system. Two primary categories of III-V semiconductor devices are -- Light-emitting diodes (LED) and microwave Integrated Circuits (IC). LEDs are fabricated from single-crystal GaAs which produce an emission band of red light. Green LEDs are generally composed of gallium phosphide (GaP).

Microwave IC devices are a specialized form of integrated circuit which is used as a high-frequency amplifier for radar, telecommunications, telemetry, as well as octave and multi-octave amplifiers for use in electronic warfare systems. Microwave IC device manufacturers typically purchase the single-crystal GaAs substrates from outside vendors.

The following is a very brief discussion of the major steps required to form and manufacture GaAs microchips at Hewlett Packard's San Jose facility. This introduction to microchips processing will help in understanding the various arsenic sources that contribute to hazardous waste generation.

Ingot Growing

As in the silicon ingot and wafer growth process, elemental forms of gallium and arsenic, plus small quantities of dopant material -- silicon, tellurium or chromium -- are reacted at elevated temperatures to form ingots of doped single-crystal GaAs.

The bulk polycrystalline GaAs compound is normally formed by the reaction of As vapor with Ga metal at elevated temperatures in sealed quartz ampoules as shown in Figure 2.1-1.

One process gaining favor in to the commercial production of bulk single-crystal GaAs is shown in Figure 2.1-2. Here, the bulk GaAs is melted and the single crystal is slowly pulled out.

The single-crystal GaAs ingot must be sandblasted and cleaned to remove exterior oxides and contaminants. The resulting ingots appear as in Figure 2.1-3.

WAFER PROCESSING

Ingot Cropping

The ends or tails of the single-crystal ingot are removed, as illustrated in Figure 2.1-4, using a water-lubricated single-bladed diamond saw, with various coolánts added to the water.

FIGURE 2.1-1
SEALED QUARTZ AMPOULE GaAs GROWTH SYSTEM

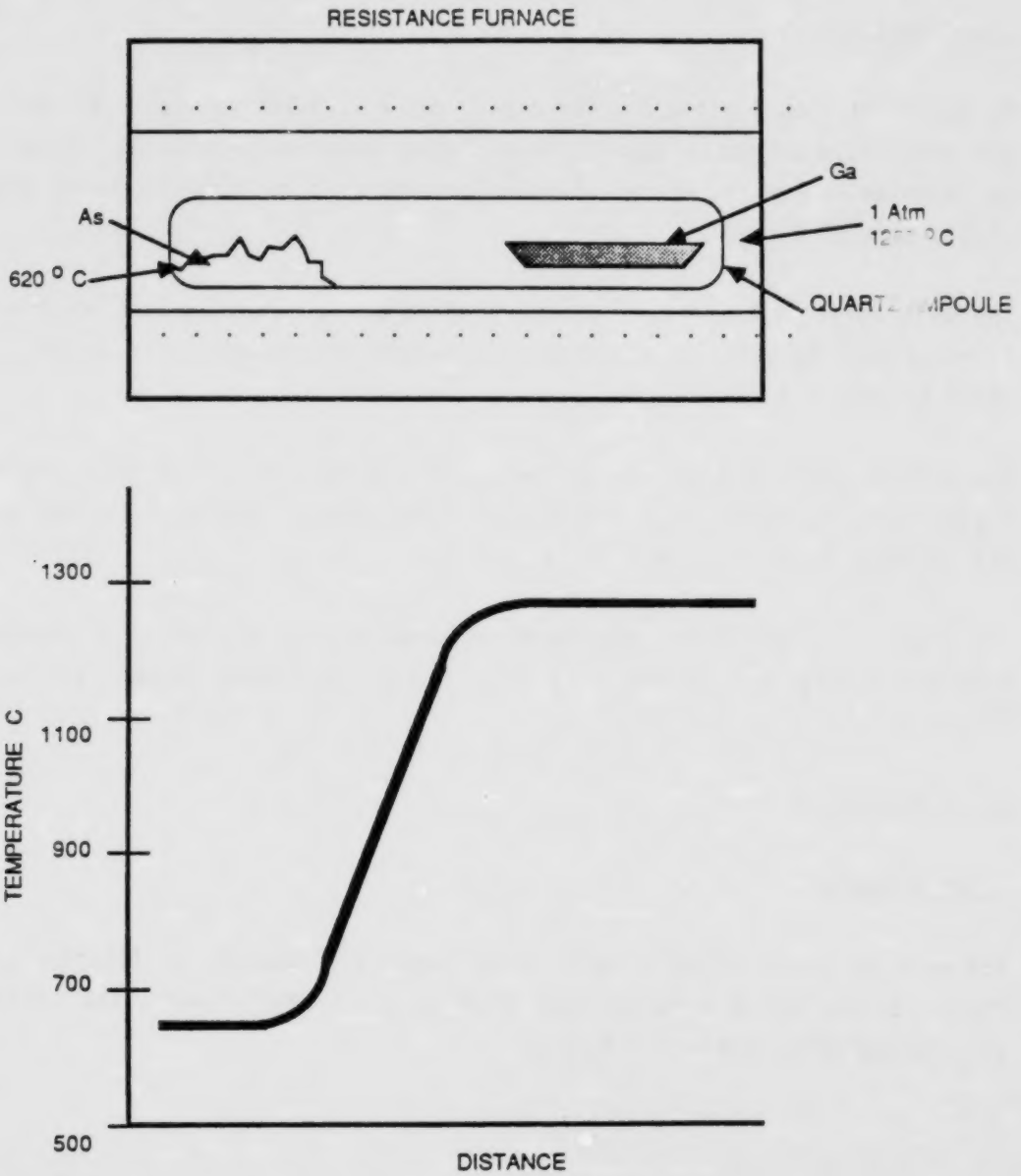


FIGURE 2.1-2
LIQUID ENCAPSULATED CZOCHRALSKI (LEC Cz) INGOT GROWTH SYSTEM 174

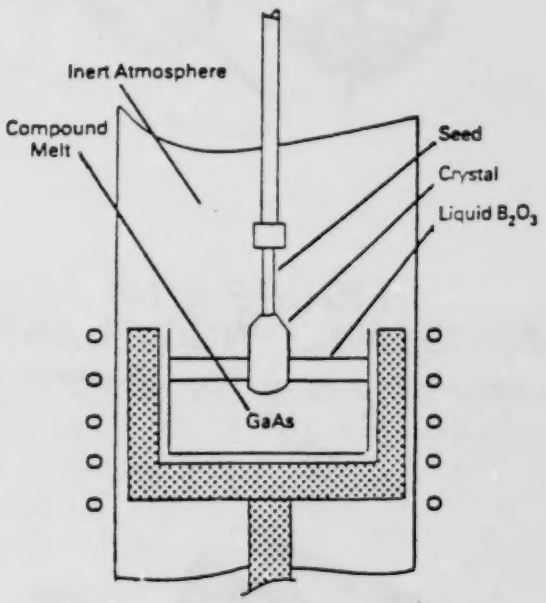


FIGURE 2.1-3
GALLIUM-ARSENIDE INGOT CRYSTALS

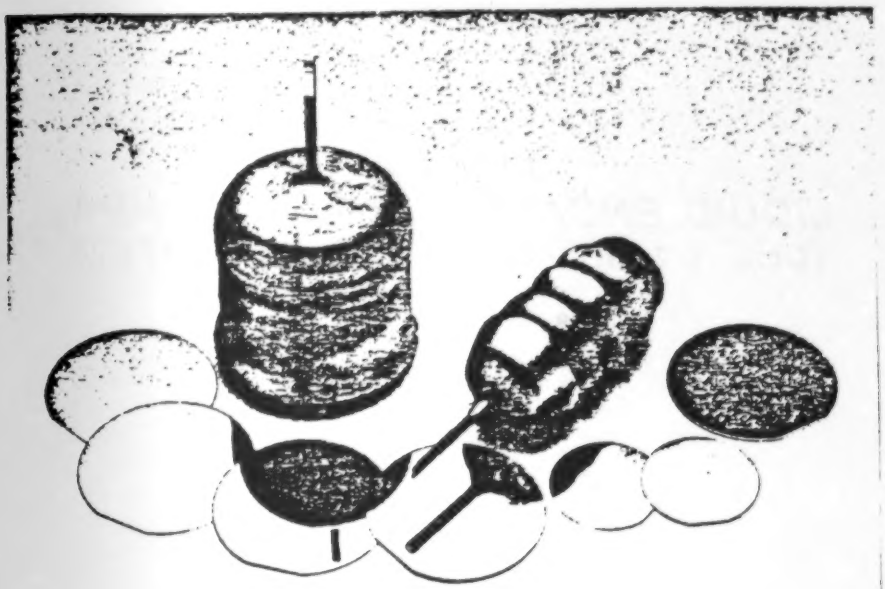
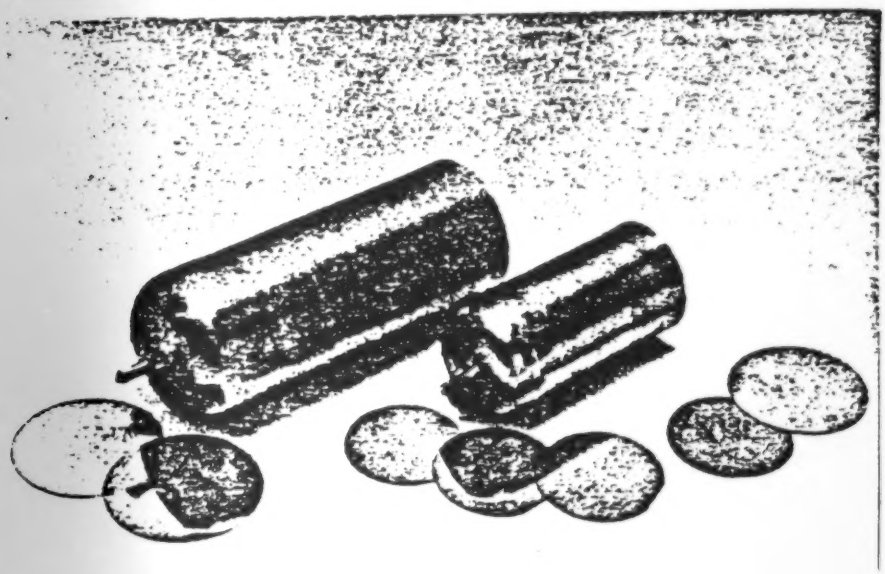


FIGURE 2.1-4
GALLIUM-ARSENIDE INGOTS AND WAFERS



Reproduced from
best available copy.

Wafer Slicing

Gallium arsenide ingots are wax mounted to a graphite beam and sawed into individual wafers through the use of automatically operated inner diameter (ID) diamond blade saws. This operation is done wet with the use of lubricants and generates a gallium arsenide slurry, which is collected and recycled.

Lapping

Wafers are wax mounted to the lapper using a hot plate, and are lapped on a machine exerting a set rotational speed and pressure. A lapping solution is fed onto the lapping surface and constitutes a slurry of aluminum oxide, glycerin and water. After a brief lapping period, the wafers are dismounted on a hot plate, rinsed in a soap solution and wiped dry.

Polishing

The wafers are then physically mounted to a mechanical polishing machine, using a sodium bicarbonate, 5% chlorine, water and colloidal silica slurry.

EPITAXIAL GROWTH

The single-crystal GaAs wafers are used as substrates for the growth of very thin layers of the same or other III-V compounds having the desired electronic or optical properties. Such crystal growth, in which the substrate determines the crystallinity and orientation of the grown layer, is called epitaxy, and a variety of epitaxial growth techniques are used in III-V display and device production.

Reactor Load and Unload

The degreased and polished wafers initially receive a PRE-EPI etch and clean step. This involves a sequential wet chemical dipping operation utilizing surfuric acid, hydrogen peroxide and water; a de-ionized water rinse; and finally, an isopropyl alcohol clean/dry.

The etch cycle is performed at the end of the growth cycle and on new quartz reactors to clean the interior surface of impurities.

Reactor Cleaning

After each growth cycle, the reactors must be opened, the wafers removed, and the lower portion of the reactor physically cleaned. The lower quartz reactor and the bottom plate (base plate) are scraped clean using a metal tool, and the particulate material (mixture of GaAs, GaAsP, arsenic oxides and phosphorus oxides) is collected in a metal container positioned below the vertical reactor.

DEVICE FABRICATION

The GaAs wafer with an epitaxially grown layer of GaAsP on the upper surface proceeds into the device fabrication processing sequence.

Wet Etching

Various mixtures of wet chemical acid solutions are used in plastic baths in locally exhausted etch stations. The primary acids in use are sulfuric hydrofluoric, hydrochloric and phosphoric. As in silicon processing, hydrogen peroxide used with sulfuric acid and ammonium hydroxide (NH_4OH) provides a caustic etch.

Backlapping

Backlapping is done to remove deposited materials from the backside of the wafer. The wafers are wax mounted to a lapper plate and wet lapped with a colloidal silica slurry.

2.2 CHEMICAL CHARACTERIZATION OF WASTE STREAMS

In order to begin any waste reduction endeavor, a complete evaluation of the chemical process must be completed. This evaluation requires the total cooperation of the facility's management, operations supervisors, operators and maintenance personnel. Hewlett Packard's - San Jose facility management and staff have exemplified total cooperation in this evaluation and have made the arsenic waste elimination an easily achievable goal.

Identification of all possible sources of arsenic required education of the Envirosphere investigators by means of written literature, lectures by Hewlett Packard's staff, and demonstrations and explanations by HP's process operating supervisors and staff. This education is one of the prime areas where HP demonstrated the kind of cooperation and knowledge of their facility and process that made the chemical characterization with respect to arsenic a rather comprehensive one.

Table 2.2-1 lists the process fluid samples and data required to be retrieved for each of the GaAs process steps thought to be contributing arsenic in HP's facility. Figure 2.2-1 illustrates how arsenic wastewater flows through that facility. Numbers listed here correspond to those on Table 2.2-1.

The first three arsenic sources were thought to be minor and composed of soluble arsenic. These waste streams flow directly to the HF preholding tank and are not involved in the Slurry Recovery process. Sample acquisition for these sources required the operator to perform the wash process in a container with graduations on the sides for volume measurement. Samples were taken after the processes were completed. Arsenic analysis was done on the measured wash solution and with this analysis and the number of ingots or wafers cleaned or etched, a total arsenic contribution was calculated.

TABLE 2.2-1

RECOMMENDED DATA AND SAMPLE ACQUISITION - HEWLETT-PACKARD

1. Ingot Cleaning (waste to HF system)	a. Obtain a 1/2 liter sample of the Aqua Regia solution plus rinse just before emptying container.
	b. Measure the volume of cleaning solution.
	c. Indicate how many ingots were cleaned in the solution sampled.
	d. Indicate how many ingots are cleaned every month.
	e. Repeat steps a through c.
	f. Have the samples analyzed for arsenic.
2. W Etch (waste to HF system)	a. Obtain a 1/2 liter sample each of the etch solutions.
	b. Measure the volume of chemical the sample was taken from and indicate how many wafers have been etched.
	c. Indicate how many wafers are etched each month.
	d. Obtain a second sample the next day and analyze both for arsenic.
3. Furnace Cleaning (waste to HF system)	a. Obtain a 1/2 liter sample of the cleaning solution. Catch the wash and first rinse solutions in a plastic container under the hood prior to sampling.
	b. Measure the volume of solution the sample was taken from and indicate how many furnaces were washed.
	c. Indicate how many furnaces are cleaned monthly.
	d. Repeat the sampling a second day and analyze both for arsenic.

TABLE 2.2-1
(Continued)

RECOMMENDED DATA AND SAMPLE ACQUISITION - HEWLETT-PACKARD

4.	Ingot Grinding (waste to slurry system) (coolant side)	a. Obtain records indicating the weight of GaAs lost per ingot while grinding and the number of ingots ground per month.
		b. Obtain the liquid throughput of each grinding machine.
5.	Ingot Cropping (waste to slurry system) (coolant side)	a. Obtain records that indicate the number of cuts per ingot and the number of ingots per month.
		b. Obtain throughput coolant volumes per cropping machine.
6.	Wafer Slicing (waste to slurry system) (coolant side)	a. Obtain records indicating how many wafers are sliced per month. This number, the width of the saw blade, and the ingot diameter will be used to calculate the GaAs sent to the slurry system per month.
		b. Confirm that slicing machine uses about 100 gal/day coolant and about 100 gal/day of city water all of which flushes the GaAs into the slurry system.
7.	Wafer Profiling (waste to slurry system) (coolant side)	a. Obtain throughput rates for profiling machines as well as average weight loss per wafer resulting from the profiling process.
8.	Lapping (waste to slurry system) (non-coolant side)	a. Obtain records that indicate average weight loss by thickness reduction and by simple weight loss of wafers before and after lapping.
		b. The throughput of liquid for each machine will be obtained as well as the length of time (hrs) each machine operates per month.
9.	Chemical/Physical Polishing (waste to slurry system) (non-coolant side)	a. Weight loss per wafer will be estimated from records based on thickness removed by polishing.
10.	Backlapping (waste to slurry system) (non-coolant side)	a. Weight loss per wafer will be determined for a least 20 wafers by weighing before and after backlapping.
		b. Obtain machine liquid flowrates.

TABLE 2.2-1

(Continued)

RECOMMENDED DATA AND SAMPLE ACQUISITION - HEWLETT-PACKARD

11.	Coolant Side Circulating Liquid	a. Obtain two 1/2 liter samples four (4) hours apart. Analyze for arsenic, then filter through 0.45 micron paper and analyze arsenic in filtrate. Lab must calculate exact percent solids of each sample based on weight of GaAs on filter paper.
		b. Have lab determine particle size distribution on each sample.
12.	Non-Coolant Side Circulating Liquid	a. Obtain two 1/2 liter samples four (4) hours apart. Analyze for arsenic, then filter through 0.45 micron paper and analyze arsenic in filtrate. Lab must calculate exact percent solids of each sample based on weight of GaAs on filter paper.
		b. Have lab determine particle size distribution on each sample.
13.	Slurry System Overflow to HF System	a. Obtain four 1/2 liter samples four (4) hours apart. Analyze for arsenic, then filter through 0.45 micron paper and analyze arsenic in filtrate. Lab must calculate exact percent solids of each sample based on weight of GaAs on filter paper.
		b. Measure the liquid flowrate until reasonably comparable rates are obtained.
14.	Preholding Tank to Holding Tank Flowrate	a. Obtain two 1/2 liter samples four (4) hours apart. Analyze for arsenic, then filter through 0.45 micron paper and analyze arsenic in filtrate. Lab must calculate exact percent solids of each sample based on weight of GaAs on filter paper.
		b. Measure the liquid flowrate until reasonably comparable rates are obtained.
		c. Measure flowrate on two(2) separate days.
		d. Obtain preholding tank volume.

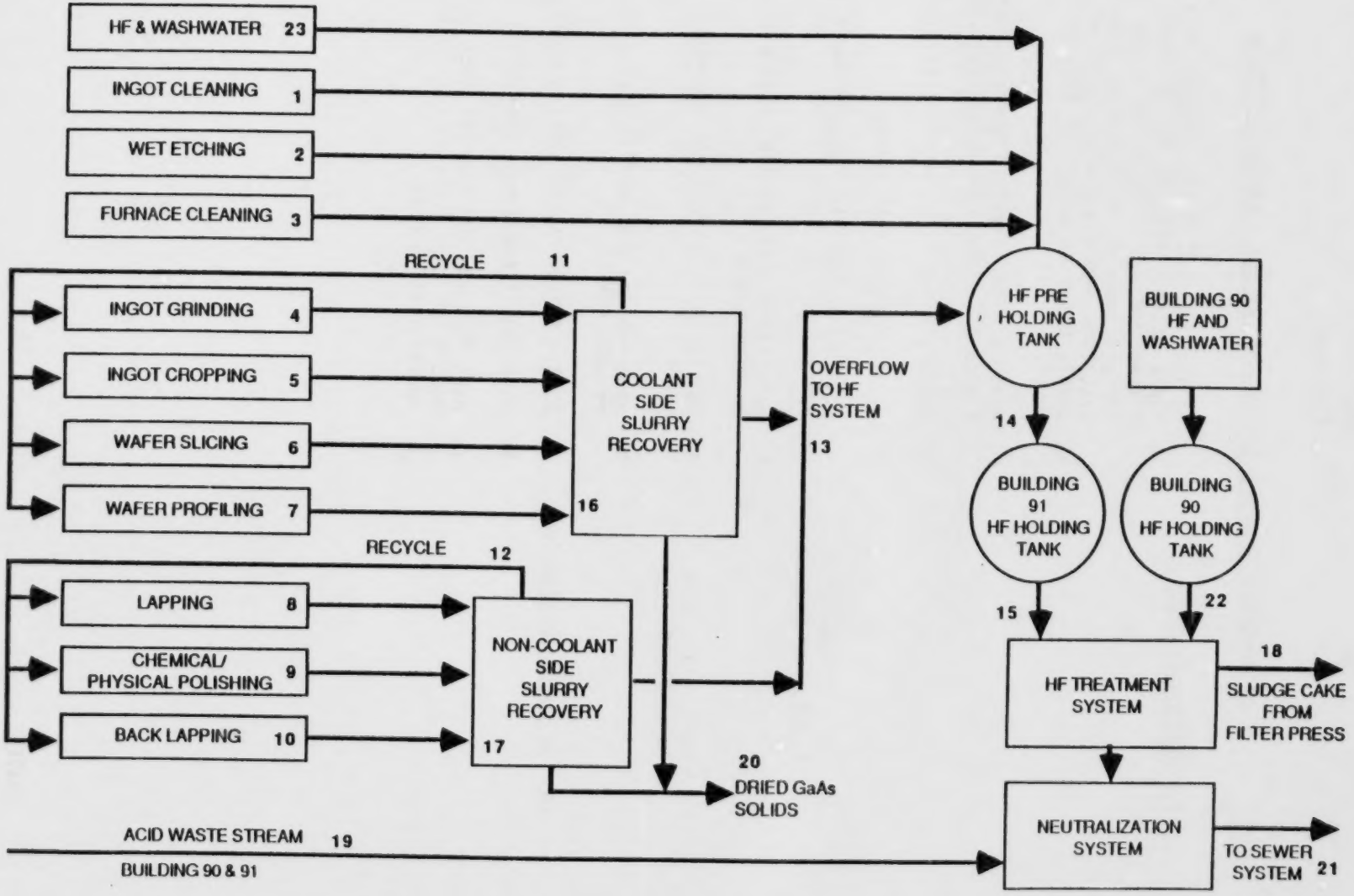
TABLE 2.2-1

(Continued)

RECOMMENDED DATA AND SAMPLE ACQUISITION - HEWLETT-PACKARD

15.	Holding Tank Output	a. Obtain two 1/2 liter samples four (4) hours apart. Analyze for arsenic, then filter through 0.45 micron paper and analyze arsenic in filtrate. Lab must calculate exact percent solids of each sample based on weight of GaAs on filter paper.
		b. Measure the liquid flowrate until reasonably comparable rates are obtained.
		c. Measure flowrate on two(2) separate days.
		d. Obtain holding tank volume.
16.	Coolant Side Inlet Fluid	a. Obtain two 1/2 liter samples two(2) hours apart.
		b. Have lab analyze partial size distribution on each sample.
17.	Non-Coolant Side Inlet Fluid	a. Obtain two 1/2 liter samples two(2) hours apart.
		b. Have lab analyze partial size distribution on each sample.
18.	HF System Sludge Cake	a. Obtain two(2) representative samples.
		b. Have EPA listed metals determined.
		c. Have the lab run the WET test on each sample as per Title 22 of California Administrative Code.

FIGURE 2.2-1
GALLIUM-ARSENIDE MICROCHIP MANUFACTURING
ARSENIC WASTEWATER FLOW DIAGRAM



11-2

Obtaining data for streams 4 through 10 involved acquisition of detailed and confidential company records that listed the average number of GaAs ingots produced per month, the average number of wafers cut from each ingot, the exact weight loss for each cropping and grinding operation, and the exact dimension change and weight loss per wafer for each manufacturing operation. Since these operations require exacting procedures and are batch type processes, it was concluded that weight loss records would provide data far superior to that obtained from liquid sampling and liquid rate measurements. Because of this decision and the fact that some of this machinery uses recycled as well as fresh water, no liquid measurements were made on streams 6 through 10.

Laboratory analysis samples taken on streams 11 and 12 were to be used to evaluate the currently active GaAs Slurry Recovery process and to provide particle distribution data for any solids recovery process (filtration) to be recommended. Flow measurements were not possible because stream 12 was not in use (no recycle) during the study period, and stream 11 recycle (although in operation) does not contribute any data toward evaluation of arsenic sources. Extensive flowrate data will be necessary only when solids recovery equipment specification and design (Step II Grant) are in progress.

Evaluation of wastestream 13 involved sampling the intake of a concrete sump pump which was equipped with a float-activated switch. Sampling was easily performed with flow rate measurement being taken from the average number of pump cycles per month and the cycle volume. Observations of pump cycle times along with the calculated flowrate confirm that this flowrate is indeed very small.

Flow measurements and laboratory samples for streams 14 and 15 were easily obtained by HP personnel. Measurements confirm that the HF and washwater contributes almost all of the 5,000 gallon per day flowrate to the HF Treatment system. Analysis of the HF and washwater for arsenic indicate that none is present in detectable amounts.

Measurements of streams 16 and 17 were made for the same reasons as streams 11 and 12. That is, for evaluation of particle size distribution and slurry recovery process evaluation. It was found that inlet fluid composition was highly dependent on which wafer manufacturing operations were being performed at the time. This obstacle led, in part, to the decision to use GaAs weight loss data on file rather than base the evaluation on such non-steady state sampling data.

Chemical analysis of the HF Treatment System Sludge Cake (#18) indicates that this material is considered to be extremely hazardous solely because of its arsenic content. Waste Extraction Tests (WET) indicate that this arsenic is in an extremely inert form and that even in its elevated concentration it produces a WET test result with a non-hazardous leachate. Our conclusion is that a 50 percent reduction in arsenic content in the sludge cake would produce a solid material classified as non-hazardous by the State of California except for fluoride content. This would result in total arsenic waste elimination at Hewlett-Packard's San Jose facility.

Arsenic analysis of the other waste streams at HP's facility completed our chemical characterization. Results are listed in Table 2.2-2 and illustrated in Figures 2.2-2, 2.2-3 and 2.2-4. Figure 2.2-2 indicates the sources and amounts of the average monthly arsenic weights that are produced at HP's San Jose facility (Table 2.2-2 data column 2). The most important point here is that nearly all (about 94%) of the arsenic that flows to the HF Treatment System is from the Slurry Recovery process and is essentially all solid GaAs particles. The remainder is entirely soluble arsenic from the cleaning and etching processes.

Figure 2.2-3 presents information tabulated in Table 2.2-2 (data column three) and illustrates the relative amounts of arsenic produced from each source with respect to GaAs solids currently recycled off site and arsenic disposed of as a hazardous waste in the sludge cake from the HF Treatment system. Daily liquid flowrates are indicated on Figure 2.2-4 and in Table 2.2-2. Here, the most important conclusion to be drawn is that a

TABLE 2.2-2

ARSENIC PROCESS WASTEWATER DATA SUMMARY

Stream Number	Stream Source	Liquid Flowrate (GPD)	Arsenic Rate (lb/MD)	Percent Arsenic to HF Treatment System and Recycled Solids	Total Arsenic Concentration (mg/L)	Percent Solids	Soluble Arsenic Concentration (mg/L)
1.	Ingot Cleaning	0.6	0.03	0.04		<0.1	
2.	Wet Etching		0.66	0.93		<0.1	
3.	Furnace Cleaning	<0.1	0.02	0.03		<0.1	
4.	Ingot Grinding	166.0	51.43	72.76			
5.	Ingot Cropping	10.2	1.43	2.02			
6.	Wafer Slicing		11.81	16.71			
7.	Wafer Profiling		0.60	0.84			
8.	Lapping		0.77	1.09			
9.	Polishing		0.23	0.32			
10.	Backlapping		3.70	5.23			
11.	Coolant Side Circulating Liquid					1.0	18
12.	Non-Coolant Side Circulating Liquid					1.1	15
13.	Overflow to HF System	7.8	11.09	15.69			
14.	Preholding Tank Output	5,000	11.80	16.69		1.0	20
15.	Holding Tank Output	5,000	11.80	16.69		1.3	20
16.	Coolant Side Inlet Fluid					6.9	210
17.	Non-Coolant Side Inlet Fluid						
18.	HF System Sludge Cake		10.85	16.69			
19.	Acid Wastestream	155,000	1.18	0.0			
20.	Slurry Recovery Solids	0	58.88	83.31			
21.	Wastewater to Sewer System	170,000	2.13	-	0.05	<0.1	0.05
22.	Building 90 HF and Wastewater			0.0	<0.5	<0.1	<0.5
23.	Building 91 HF and Wastewater			0.0	<0.5	<0.1	<0.5

FIGURE 2.2-2
GALLIUM-ARSENIDE MICROCHIP MANUFACTURING
ARSENIC PROCESS WASTE FLOW DIAGRAM
ARSENIC PRODUCTION RATES

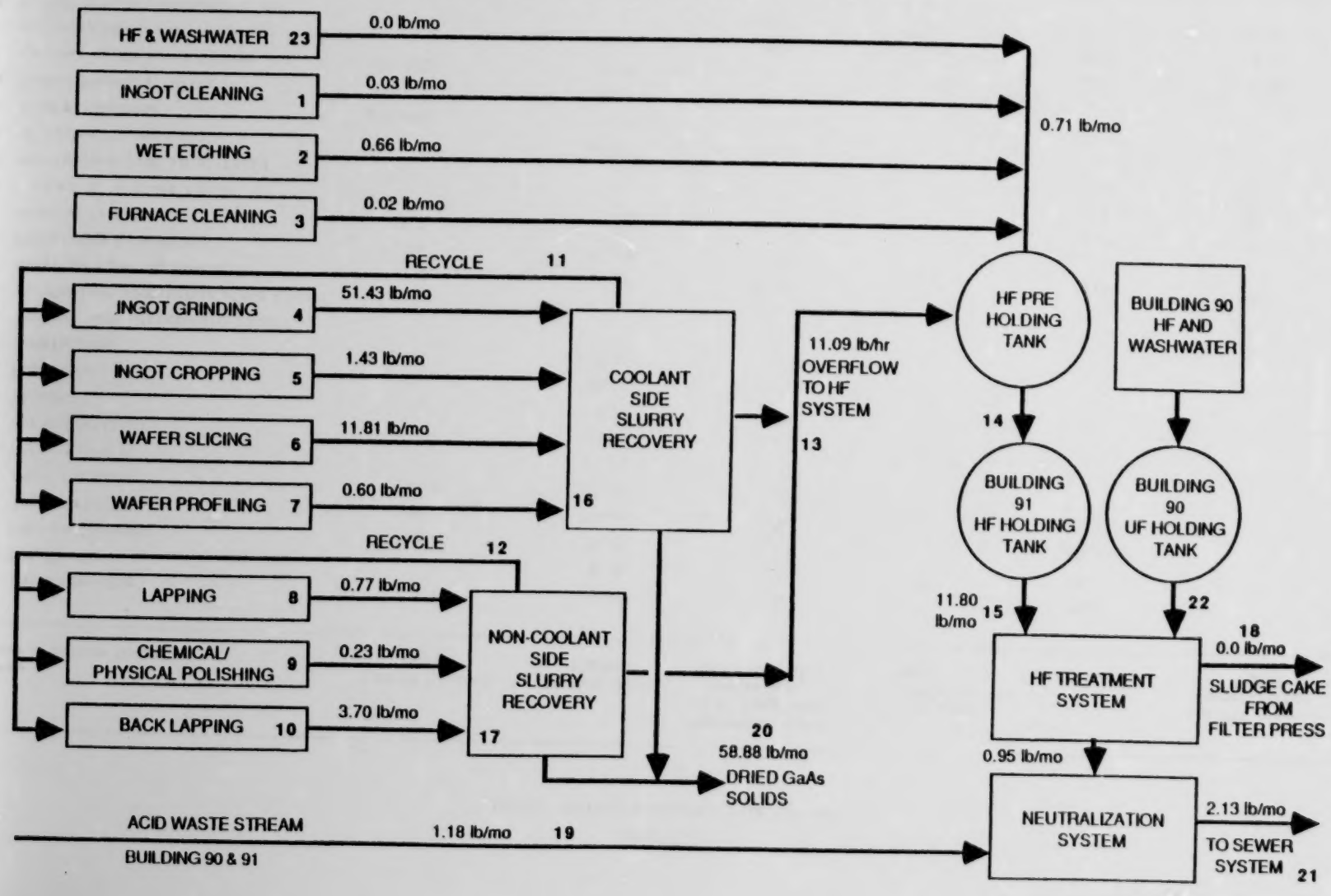


FIGURE 2.2-3
GALLIUM-ARSENIDE MICROCHIP MANUFACTURING
ARSENIC WASTE WATER FLOW DIAGRAM
PERCENT ARSENIC TO HF TREATMENT SYSTEM AND RECYCLED SOLIDS

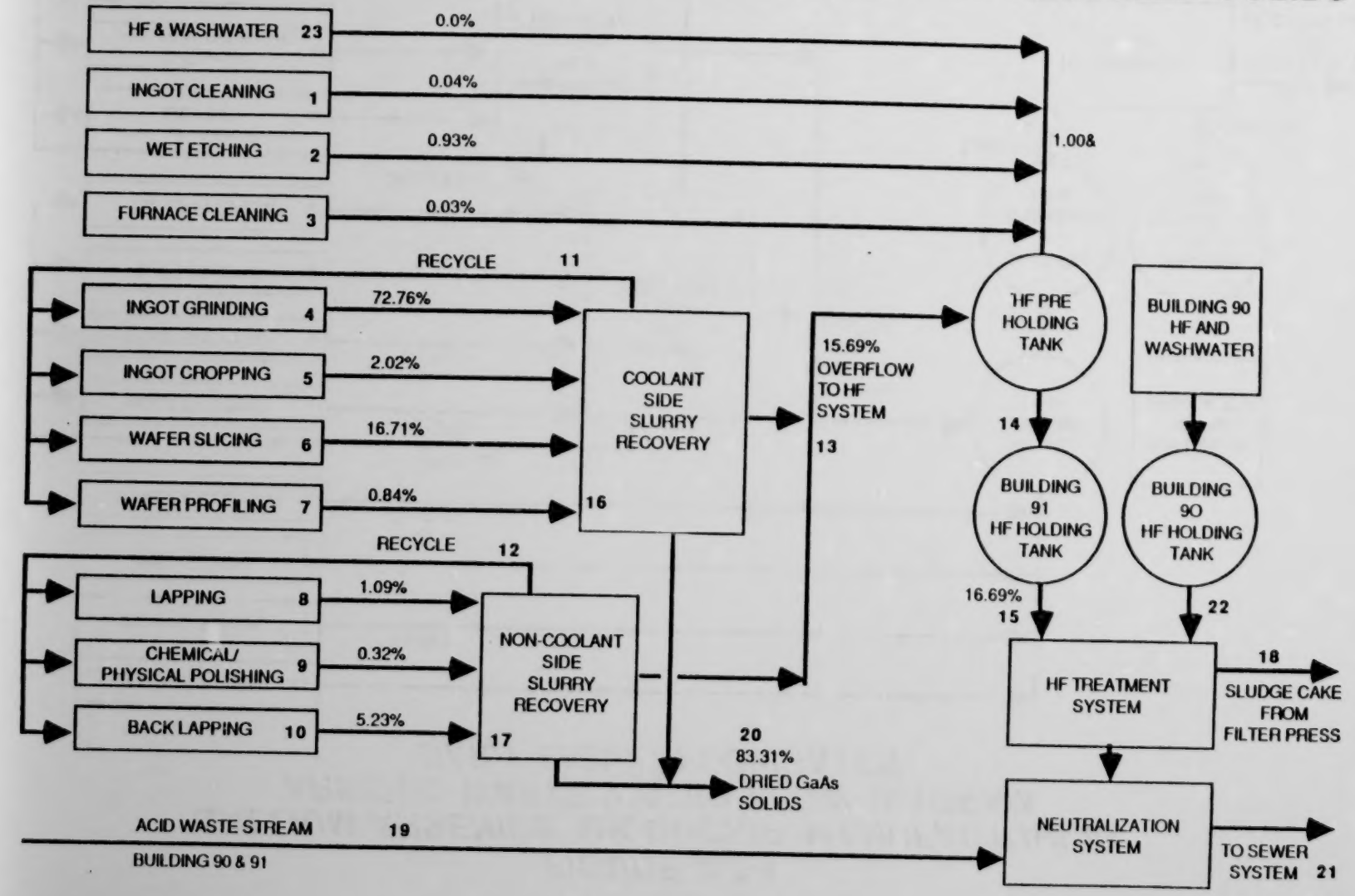
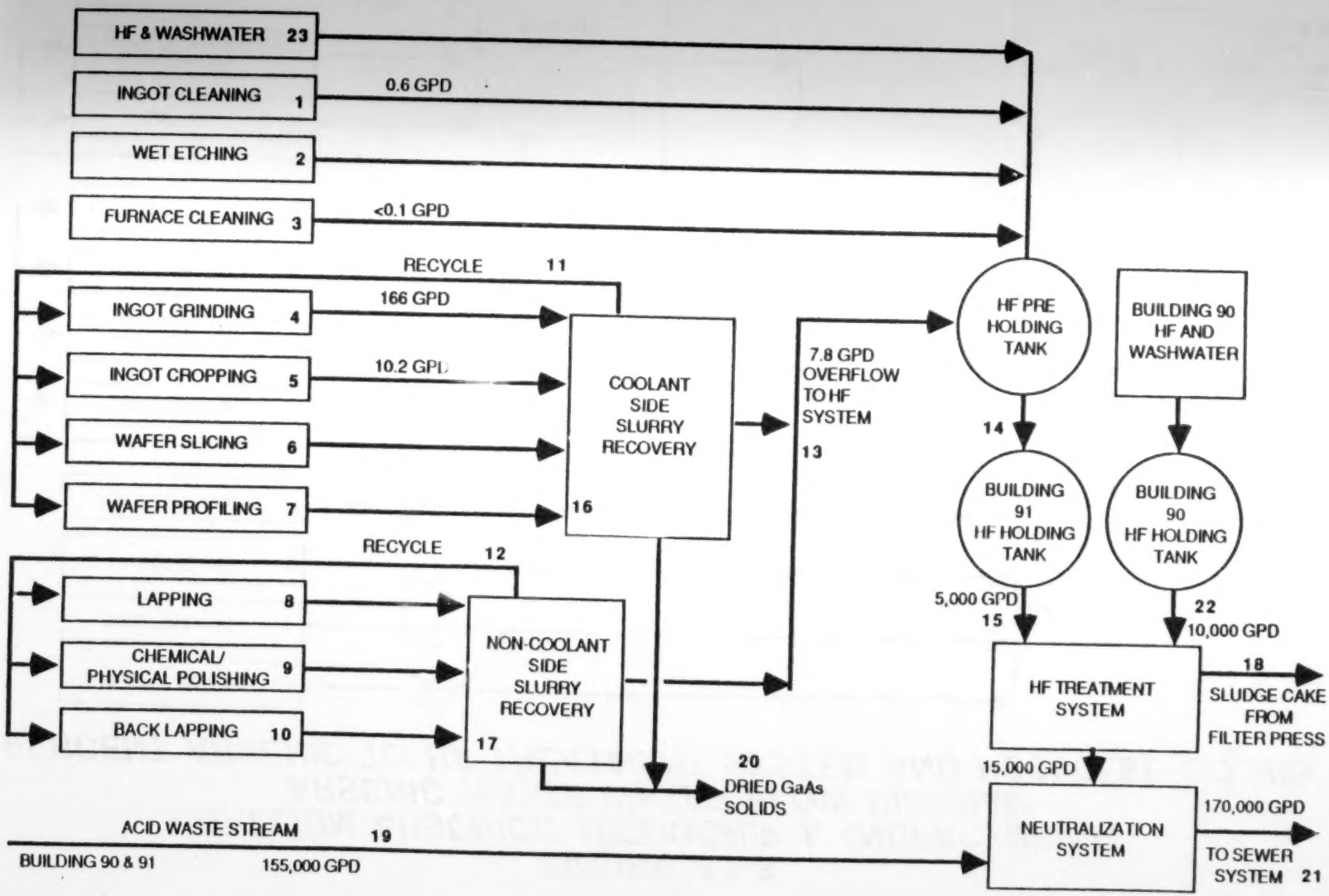


FIGURE 2.2-4
GALLIUM-ARSENIDE MICROCHIP MANUFACTURING
ARSENIC WASTE WATER FLOW DIAGRAM
DAILY LIQUID FLOWRATES



waste stream with a flowrate of approximately eight (8) gallons per day of GaAs-laden liquid overflowing to the HF Treatment System is responsible for about 94 percent of the arsenic in the sludge cake solids.

Considerations of other wastewater streams such as the Building 90 HF and Washwater and the Acid Waste stream were made but either the arsenic content was confirmed by analysis to be below detection limits or it did not fall within the scope of this investigation. In either case, the levels are very low and do not present a potential arsenic contamination source. In fact, the wastewater treatment systems in place at HP's San Jose facility produce a wastewater stream to the sewer system at least 20 times lower than this discharge permit allows.

In summary, arsenic solids (GaAs) represent at least 94% of the arsenic contamination found in the sludge cake produced from the HF Treatment process. These solids are produced from physical sawing, grinding and polishing operations and are present in the overflow liquid from the Slurry Recovery process. Removal of these solids from this water flowing to the HF Treatment process by a filtration technique appears to be the most direct and simple process from a chemical engineering point of view. Although filtration is possible, a review of other arsenic removal processes is important. In order to choose the best system for arsenic recovery, a working knowledge of arsenic chemistry is required. This knowledge, along with information regarding potential arsenic removal processes, should be considered before correct engineering design of the wastewater treatment system can be initiated. Detailed discussions of both areas follow.

2.3 ARSENIC CHEMISTRY

Arsenic is a member of the nitrogen family of chemical elements which is composed of Nitrogen (N), Phosphorous (P), Arsenic (As), Antimony (Sb) and Bismuth (Bi). Each of these elements has five valence electrons per atom. There is a tendency in these elements to take up electrons from the more metallic elements for form triply charged negative ions. Nitrogen forms nitride ion, N^{---}, on reaction with certain active metals, and phosphorous somewhat less readily forms phosphide ion, but the other members of the group show little or no inclination in this direction. This is in accord with the general tendency for the elements of a family to become more metallic with increasing atomic number. This same trend is reflected in the order of decreasing ionization potentials and decreasing relative electronegativities ---N > P > As > Sb > Bi.[1]

The elements of the nitrogen family form hydrides of the general formula MH_3. They also form oxides in which the element is in the +3 or +5 oxidation state.

The physical properties of the free elements show a regular graduation from nonmetallic to metallic with increasing atomic number. Like the first members of other families, nitrogen differs in many respects from the other members of its family.[1]

Some of the general trends in the nitrogen family are summarized in Table 2.3-1.

Arsenic and antimony occur more widely, though in lower total abundance, and are often associated with sulfide minerals, particularly those of Copper, Lead and Gold.

2.3.1 ELEMENTAL ARSENIC

The normal form of As, is bright and metallic in appearance and has crystal structure similar to that of black Phosphorous. The metal burns in air

TABLE 2.3-1

TRENDS IN PROPERTIES OF THE ELEMENTS OF THE NITROGEN FAMILY (1)

NH_3	PH_3	AsH_3	SbH_3	BiH_3
Decrease in Basic Character - Decrease in Stability				
N_2O_3	P_4O_6	As_4O_6	Sb_4O_6	Bi_2O_3
Acidic Decrease in Acidic Character				
N_2O_5	P_4O_{10}	As_4O_{10}	Sb_4O_{10}	Bi_2O_6
Strongly Acidic Decrease in Acidic Character				Weakly Acidic
NCl_3	PCl_3	$AsCl_3$	$SbCl_3$	$BiCl_3$
Increase in Ionic Character -- Decrease in Ionization Potential				

on heating to form the oxide, and it reacts directly and readily with halogens and some other nonmetals. Dilute non-oxidizing acids are without effect on it, but with strong acids such as nitric acid, arsenic acid is produced [2].

Arsenic combines readily with many nonmetals and also reacts with many metals to form compounds called arsenides. In moist air, arsenic oxidizes to form arsenic trioxide (As_4O_6).

2.3.2 COMPOUNDS OF ARSENIC

The trioxide, As_4O_6 is the common oxide of arsenic. As_4O_{10} is a white solid that decomposes with heat into the trioxide and oxygen.

Arsenic forms two series of acids, the arsenious and arsenic acids, which are somewhat similar to the acids of phosphorus. A water solution of As_4O_6 is called arsenious acid; the oxide, however, is not very soluble. Arsenic acid, H_3AsO_4, is prepared by the oxidation of As_4O_6 with nitric acid [3].

$$As_4O_6 + 4\ HNO_3 + 4\ H_2O \rightarrow 4\ H_3AsO_4 + 2\ N_2O_3\ \uparrow$$

The two halides that are formed by arsenic, $AsCl_3$ and AsF_5, hydrolize less readily than the corresponding halides of phosphorus.

Three sulfur compounds of arsenic have been discovered, but they are not important commercially. They are arsenic disulfide, As_2S_2, arsenic trisulfide, As_2S_3 and arsenic pentasulfide, As_2S_5. They can be prepared by heating a mixture of arsenic and sulfur in the calculated amounts. Arsenic trisulfide is a yellow crystalline solid that can be precipitated from solution by H_2S.

$$2\ H_3AsO_3 + 3\ H_2S \rightarrow 6\ H_2O + As_2S_3\ \downarrow$$

The pentasulfide, As_2S_5, a yellow solid, can be precipitated from a solution of arsenic acid by H_2S.

$$2\ H_3AsO_4 + 5\ H_2S \rightarrow 8\ H_2O + As_2S_5 \downarrow$$

Arsenic forms thio acids and their corresponding salts. Soluble sulfides such as Na_2S and $(HN_4)_2S$ are used in chemical analysis to dissolve the sulfides of arsenic and thus separate them from a mixture of metal sulfides (3).

$$3\ Na_2S + As_2S_3 \rightarrow 2\ Na_3AsS_3 \} \text{ soluble}$$

$$3\ Na_2S + As_2S_3 \rightarrow 2\ Na_3AsS_4 \} \text{ soluble}$$

The insoluble metal sulfides are separated by filtration and the arsenic sulfides are recovered by treating the filtrate with HCl (3).

$$2\ Na_3AsS_3 + 6\ HCl \rightarrow 6\ NaCl + As_2S_3 \downarrow + 3\ H_2S \uparrow$$

Arsine, AsH_3, is formed by the action of hydrogen on compounds of arsenic.

$$12\ H_2 + As_4O_6 \rightarrow 6\ H_2O + 4\ AsH_3 \uparrow$$

Arsine has a garliclike odor and, like all arsenic compounds, is extremely poisonous. The gas burns in oxygen and forms the trioxide and water.

$$4\ AsH_3 + 6\ O_2 \rightarrow 6\ H_2O + As_4O_6$$

At high temperatures, arsine decomposes into its elements.

$$4\ AsH_3 \rightarrow 7\ H_2 \uparrow + As_4$$

The hydrogen compounds of arsenic, corresponding to the general formula MH_3, have electronic and geometric structures analogous to those of ammonia and phosphine.

Arsine is definitely poisonous, even in small amounts[1].

Arsine like the others in this group is prepared by either the hydrolysis of metallic arsenides

$$Na_3As + 3H_2O = 3Na^+ + 3OH^- + AsH_3$$

or by the reduction, by active metals in acid solution, of compounds of arsenic in the higher oxidation states. When, for example, a solution of a soluble arsenite in dilute sulfuric acid is treated with metallic zinc, arsine gas is produced and is evolved along with the hydrogen formed by reaction of the zinc with the acid [1].

$$AsO_3^{---} + 9H^+ + 3Zn = AsH_3 + 3Zn^{++} + 3H_2O$$

The reaction just described, along with the relatively easy thermal decomposition of arsine, constitutes the basis for an exceptionally sensitive test for arsenic, known as the Marsh test. A solution of the substance to be tested is introduced into a flask containing zinc (or some other active metal) and an acid. If arsenic is present, arsine gas is produced. If the arsine gas is heated, it decomposes to give a shiny black mirror-like deposit of elemental arsenic[1].

Arsenic forms both +3 and +5 sulfides with the formulas As_2S_3 and As_2S_5, respectively. These are usually obtained by precipitation with hydrogen sulfide according to the following equations.

$$2H_3AsO_4 + 5H_2S = As_2S_5 \downarrow + 8H_2O$$

$$2SbCl_3 + 3H_2S = Sb_2S_3 \downarrow + 6H^+ + 6Cl^-$$

The arsenic sulfides are yellow in color and are soluble in concentrated acids. The sulfides, like the oxides, are soluble in basic solutions, but of particular interest is their ready solubility in solutions of sulfides or hydrosulfides to yield the thioarsenites AsS_3 and AsS_4.

These reactions are used in many qualitative analytical procedures for the separation of the sulfides of arsenic from the sulfides of mercury, lead, copper, bismuth, and cadmium.

Arsenic also forms a sulfide having the molecular formula As_4S_4, which provides an interesting example of the fact that the molecular formula of a compound does not necessarily provide any indication as to the valences of the atoms involved[1].

2.3.3 PHYSICAL - CHEMICAL ASPECTS

Compounds of arsenic in various chemical forms have most prominently figured in the extensive history of the toxicology of the element. Geochemically, arsenic is encountered as a component of sulfidic ores, occurring as the arsenides and diarsenides of metals such as nickel, cobalt, and copper, and is present in rocks and soils at trace levels. Smelting of commercially important metal ores, therefore, often has associated with it the release into the environment of significant quantities of certain arsenic compounds. For example, arsenic trioxide, As_2O_3, a major form of the element in terms of its toxicological history, is a smelter product arising from air roasting of metallic arsenides or arsenic-containing sulfides[25]. Arsenic trioxide, white arsenic, is only slightly soluble in water and other solvents which do not promote chemical transformation. Its solubility in solvents which mimic physiological media may not necessarily be the same as for simple solvents, e.g., gastric juice versus water. Arsenic trioxide sublimes, the process becoming pronounced at 135°C. This property appears to have been overlooked through the years in considering analytical methods for measuring levels of the compound. Dissolution of the trioxide in aqueous media leads to formation of arsenous acid, H_3AsO_3, while alkaline treatment leads to formation of the arsenite ion, $AsO(OH)_2^-$,

with both the acid and the salt being freely soluble in a number of solvents[25].

Arsenic pentoxide, As_2O_5, may be readily prepared by nitric acid oxidation of elemental arsenic or the trioxide. Compared to the trioxide, the pentoxide has considerable solubility in water (63.0 g/100 g water), presumably dissolving to form the relatively strong arsenic acid H_3AsO_4[25].

The relative stability of solutions of arsenic or arsenous acids to oxidation-reduction is of considerable importance in terms of valency-dependent arsenic toxicity. In oxygenated media, one would expect the pentavalent form to dominate, while reducing media would favor the trivalent state[25].

Arsenous and arsenic acids both form mono-, di- and tri-metal salts, the alkali-metal salts such as potassium and sodium arsenite being freely soluble in water and the alkaline salts such as calcium or magnesium arsenite being slightly soluble[25].

While tri-organic esters of the tri- and pentavalent arsenic acids are known, they are labile to hydrolysis and one would expect the mono- and di-organic derivatives to be even more so. This behavior has implications in the postulated role of arsenate ions in interfering with phosphorylation reactions[25].

Arsine (arsenic trihydride, AsH_3) is a strong hemolytic toxicant and probably the most poisonous of the arsenicals. Although generally a minor factor in the environmental chemistry of arsenicals, it can form under certain restricted conditions, i.e., via reduction in the presence of an active hydrogen-generating source[25].

Monomethyl and dimethyl arsenic, in the form of methylarsonous and methyl arsenic, dimethylarsinous and dimethylarsinic (cacodylic) acids, occur both in the environment and are formed via *in vivo* transformation in many mammalian species, including man. Such organic arsenic compounds are also of commercial significance. For instance, both methylarsonic and

dimethylarsinic acids, usually in the form of the mono- or dialkali salts,are employed as herbicides which, when released into the environment, may undergo reduction to the corresponding labile arsine compounds, CH_3AsH_2 (methylarsine) and $(CH_3)_2$ AsH (dimethylarsine). Like trivalent inorganic arsenic, methylarsonous acid can interact with thiol groups (as can cacodylic acid) to form the CH_3-As(-S-)$_2$ and $(CH_3)_2$-As-S groups, respectively. The physical forms of arsenic in the environment depend on its mode of emission and subsequent interactions with other materials[25].

Arsenic, along with other trace metals, can be mobilized in association with airborne particles derived from high-temperature sources such as fossil-fueled power plants, metallurgical smelters and blast furnaces[25].

Arsenic compounds form insoluble complexes with soils and sediments. With soils, the interaction involves clay surfaces containing amorphous aluminum or iron oxides[25].

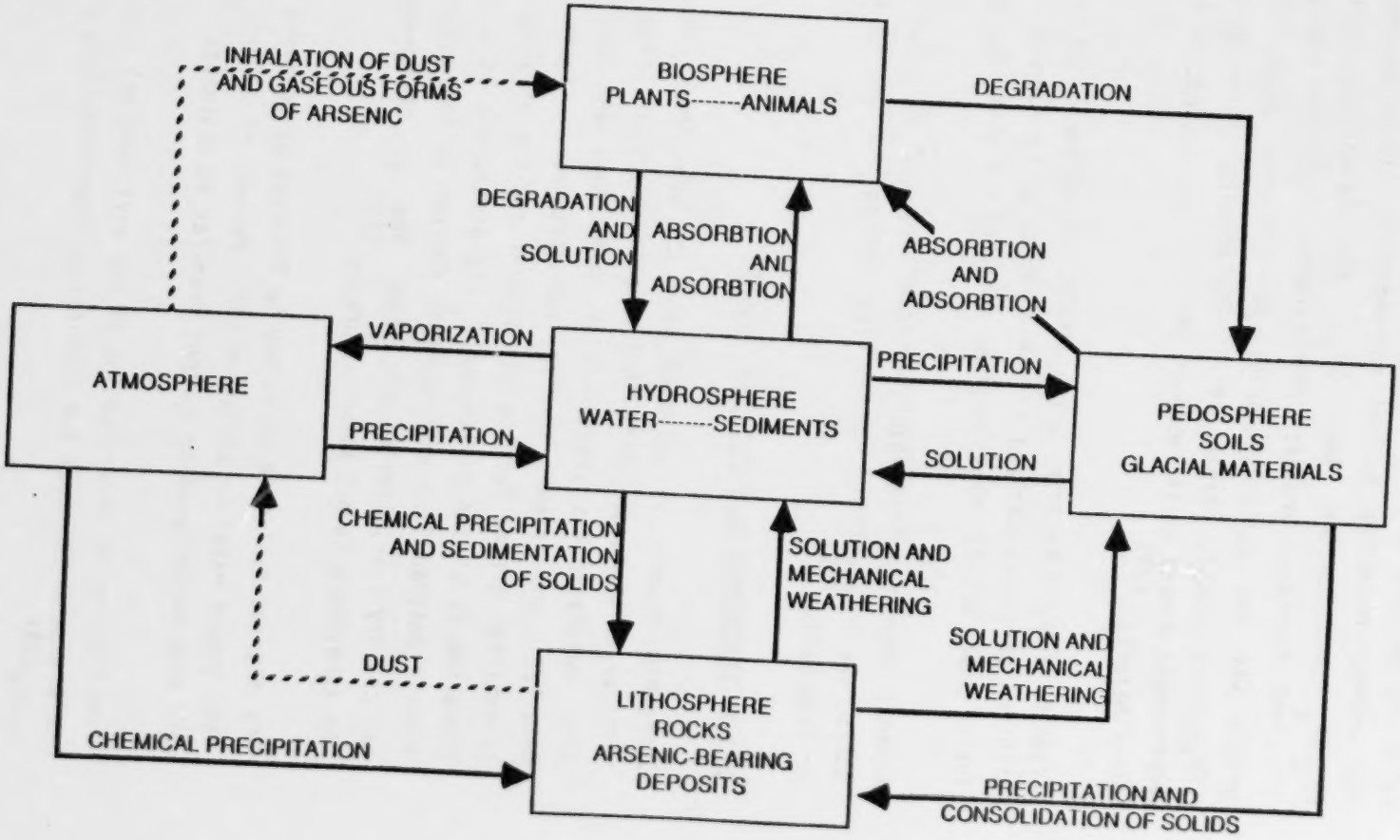
2.3.4 ENVIRONMENTAL CYCLING OF ARSENIC

Inorganic arsenic is released into the environment from a number of anthropogenic sources which include primary copper, zinc and lead smelters, glass manufacturers (specifically those that add arsenic to the raw materials) and arsenic chemical manufacturers. Figure 2.3-1 presents a generalized scheme for the geochemical cycling of arsenic through various compartments of the environment. The atmosphere is a major conduit for arsenic emitted from anthropogenic sources to the balance of the cycle via wet and dry precipitation processes. The rate of movement of arsenic from the atmosphere is not known at present[25].

Dry and wet fall onto soils may be followed by movement through soils either into ground water or surface water. Passage of arsenic into surface waters may then be followed by further transfer to sediments[25].

Complicating an understanding of the environmental cycling of arsenic is the existence of chemical and biochemical transformations which occur within the cycle[25].

FIGURE 2.3-1
THE GENERALIZED GEOCHEMICAL CYCLES FOR ARSENIC (25)



23.a

Trivalent arsenic in the atmosphere can undergo oxidation to the pentavalent state. Such conversion can also occur in aerated surface waters. On the other hand, pentavalent arsenic in an aqueous medium which is somewhat acidic is an oxidant, and, in the presence of oxidizable material, it will react to form trivalent arsenic[25].

Reduction and methylation of inorganic arsenic occur only to a limited extent in soils, 1-2 percent over a period of months having been reported in one study[25].

In terms of the relative amounts of arsenic partitioned among the various environmental compartments, Suta (1980) has calculated that land is the major sink for arsenic, accounting for approximately 90 percent of the dissipation for the year 1974. The atmosphere accounts for 7-8 percent dissipation with the least quantity appearing in waterborne effluents[25].

2.3.5 HEALTH EFFECTS OF ARSENIC AND COMPOUNDS

Arsenic, may present a health hazard to humans when it is released into the environment as a consequence of industrial processes. The preponderance of clinical and epidemiological evidence regarding the effects of arsenic pertains to trivalent inorganic arsenic. Much of this evidence suggests that trivalent inorganic arsenic is a carcinogen. Some limited evidence suggests that pentavalent inorganic arsenic may also be carcinogenic.

The main routes by which arsenic enters the human body are inhalation and ingestion. Experimental studies show that following injection of trivalent inorganic arsenic, arsenic is concentrated initially in the liver, kidneys, lungs, and spleen. After 24 hours the level in the liver and kidneys decreases, while that in the skin increases.

Both trivalent and pentavalent arsenic are mutagenic and teratogenic in animal tests. Attempts to induce tumors in experimental animals by arsenic usually have been unsuccessful, although, significantly in some instances, positive results have been obtained. Animal toxicity studies indicate that trivalent arsenic is several times more toxic than pentavalent arsenic.

Epidemiological studies of smelter workers show excess lung cancer risk in individuals exposed to arsenic trioxide, and several studies indicate that the risk increases with increasing duration and level of exposure. Risk increases of up to 8-fold have been reported. It is possible that the increased risk is not due to arsenic alone, since smelter workers are exposed concomitantly to sulfur dioxide and other toxic substances. Workers engaged in the manufacture of arsenical pesticides also showed elevated risk for pulmonary cancer. Such workers, though not exposed to sulfur dioxide, may be exposed to other toxic substances. Similar results have been recorded in vineyard workers in France and Germany, where the workers were exposed to pesticides containing trivalent and pentavalent arsenic. In the United States, agricultural workers exposed to lead arsenate spray (pentavalent) evidenced excess lung cancer associated with this process.

The currently available experimental and epidemiological evidence does not provide an adequate basis for gauging the effects of chronic low-level exposure to arsenic compounds. A clear dose-response effect has been noted in a large-scale study in which ingestion of drinking water containing arsenic was associated with subsequent development of skin cancer. It is reasonable to assume that smaller dosages of inhaled arsenic could be involved with the development of cancer, since inhalation is a more efficient route of entry to the body than ingestion. In addition, as noted above, dose-response relationships have been reported in smelter workers. Toxic effects of arsenic on humans through ingestion, injection and inhalation are furnished in Table 2.3-2.

It is difficult to determine a specific level of exposure associated with a specific level of risk because the precision of ambient air measurements is low; the level may be incorrect by as much as one order of magnitude. Nevertheless, the air levels yielding standard mortality ratios of 800 (i.e., an 8-fold increase in lung cancer deaths) have been estimated at 23 to 323 µg of arsenic per cubic meter of air.

American Conference of Government-Industrial Hygienists Inc.[4] have determined a threshold limit (TLV) of 0.2 mg per cubic meter of air. The toxic effects of arsenic on humans is shown on Table 2.3-2.

TABLE 2.3-2
TOXIC EFFECTS OF ARSENIC [a]

Compound	Route of entry	Acute effects
Trivalent inorganic arsenic	Ingestion	Throat constriction, difficulty swallowing, violent abdominal pain, vomiting, muscular cramp, possible death within 1-4 days
		Fatty infiltration of cells (especially liver cells); direct toxic action on cardiac muscle; ECG abnormalities
Arsphenamine	IV injection	Stomatitis, albuminuria, jaundice, blood dyscrasias, dermatitis, severe cerebral symptoms, acute hepatitis, ascites
Arsine	Inhalation	Enlargement of the liver, hemoglobinuria, jaundice, hemolytic anemia, abdominal pain, vomiting; acute uremia is a common cause of death (from 4th day onwards); fatty degeneration of cells, particularly those of the liver, kidneys, and cardiac musculature
		Chronic effects
Inorganic arsenic	Ingestion	Nausea, vomiting, conjunctivitis and catarrhal state of exposed mucous membranes of the nose, larynx and respiratory passages, keratoses, melanosis
	Inhalation	Perforation of the nasal septum; Rönnskär Disease (chronic "rhino-pharyngo-tracheo-bronchitis") hepatitis, jaundice, peripheral neuritis

[a] Source: Buchanan (1962).

Arsenic compounds such as the arsenites are important herbicides, calcium and other arsenates are insecticides; sulfides are pigments, rodenticides and used in pyrotechnics; gallium arsenide is in semiconductors; arsenic trichloride is employed in chemical synthesis; the gaseous tri- and pentafluorides apparently have no important commercial uses. Many organic arsenic compounds, however, have been employed in medicine, or as war gases[4].

As with other metallic poisons, the toxicities, especially the acute toxicities, of arsenic compounds are related to their solubility in water. Thus most arsenates and arsenites are acute poisons, while the sulfides are probably less toxic in an acute sense, but may be equally hazardous on prolonged exposure. Elemental arsenic is also less acutely toxic than its oxides, except for the rare yellow arsenic which is highly toxic, possibly similar to yellow phosphorus in some of its properties[4].

Systemic arsenic poisoning is rarely seen in industry, and still more rarely is it severe in character. It is hard to explain the difference between industrial and nonindustrial arsenic poisoning, but such variation is recorded in all industrialized countries. The usual effects on workers are local, on skin and mucous membranes, etc. A hoarse voice is characteristic of an arsenic worker, and a perforated nasal septum is a common result of prolonged inhalation of white arsenic dust or fume. A few documented cases of cirrhosis of the liver, however, due to occupational exposure to arsenic, have been recorded[4].

Although the epidemiologic evidence is not complete, arsenic is considered by some to be a carcinogen, certainly of the skin, and perhaps of the bronchi. Cancers from exposure to arsenic have followed: 1) the internal use of Fowler's Solution, an aromatic solution of potassium arsenite; 2) inhalation and skin contact with sheep-dust, a mixture of sodium arsenite and sulfur; 3) the combined inhalation of As_2O_3, SO_2 and other particulates from the smelting of ores containing arsenic. Experimental cancers in animals have not been produced from As_2O_3 despite several attempts and the conclusion of Vallee, et al. was that "it is improbable

that arsenic (per se) plays a significant role in the generation of cancer." The belief that other occupational factors are necessary for the development of cancer, in addition to arsenic exposure, has been expressed by others[4].

A search of the world literature reveals no reports of industrial or experimental exposures solely to arsenic compounds which contain both environmental and toxicological criteria from which a TLV can be unequivocally based. Watrous and McCaughey found concentrations of arsenic in a pharmaceutical plant averaging about 0.2 mg/m^3, with no definite evidence of intoxication. Pinto and McGill studied a group of smelter employees and found an average urinary arsenic excretion of 0.8 mg/L. The chief manifestation of toxic exposure was dermatitis, with perforation of the nasal septum, pharyngitis and conjunctivitis noted less frequently. A reasonable interpretation of the urinary arsenic levels would indicate an average exposure of about 0.2 mg/m^3 of arsenic in air. Since individual concentrations as high as 4 mg/L of urine were found, it is probable that many workers were exposed at higher concentrations[4].

In its criteria document for inorganic arsenic, NIOSH in 1973 recommended 0.05 mg As/m^3 (as a TWA) as a workplace air standard. This was changed in 1975 to 0.002 mg/m^3 as a 15 minute ceiling[4].

The first limit was based primarily on reports of cancer among workers exposed to arsenic, as well as non-occupational cancer resulting from arsenic medications. The only pertinent environmental data cited not already noted consist of an average concentration of 0.56 mg/m^3 computed from the paper from Perry et al on an English sheep dip factory study, and a study by Lee and Fraumeni in a smelting plant. Concentrations of 1.47, 1.50 mg/m^3 were reported in "medium and high exposure area" and 0.65, 0.17 and 0.002 mg/m^3 in "light exposure areas". In both plants an increased incidence of cancer was reportedly found[4].

There appears to be no published explanation of the reasons for the reduction of the NIOSH 1973 recommendation of a TWA of 0.05 mg/m^3 as a standard, to a ceiling of 0.002 mg/m^3 in 1975[4].

Normal values of arsenic in urine, as recorded in the literature, vary from 0.013 to 0.046 mg/L, to 0.13, to 0.025 mg/L. The urinary excretion, in mg/liter, of elements that are freely eliminated by this route, such as fluorine, mercury and arsenic, is at most 2.5 to 5 times the occupational exposure in mg/cubic meter of air. It is apparent that biological monitoring for arsenic by urinalysis would be of limited value in determining whether or not the NIOSH recommended standard was being met or exceeded[4].

According to the 1977 compilation of occupational exposure limits of the International Labor Office, the following countries had adopted the previous TLV of 0.5 mg/m^3: Australia, Finland, Japan, Holland, Switzerland and Yugoslavia. Czechoslovakia, East Germany, Hungary and Poland specified the USSR MAC of 0.3 mg/m^3; Romania 0.2 and Sweden 0.05 mg/m^3. Only three of 18 countries (West Germany, Italy and Sweden) designated arsenic and compounds as carcinogens, although Belgium and the Netherlands so characterized arsenic trioxide[4].

It is possible that some arsenic compounds, the trichloride for example, might produce certain toxic effects at concentrations below 0.2 mg/m^3 of arsenic. Data to substantiate this speculation are lacking. The contrary situation, that some compounds, or the metal itself, are chronically less toxic than As_2O_3, the form for which most information is available, seems more probable in the light of present knowledge. Therefore, a TLV of 0.2 mg As/M^3 for soluble compounds of arsenic is recommended[4].

2.4 IDENTIFICATION OF POTENTIAL TREATMENT PROCESSES

2.4.1 INTRODUCTION

The primary goal in hazardous waste reduction in a chemical process facility is to accomplish the task without impacting the process itself and to, if possible, generate a saleable product that has been generated from the waste reduction "treatment".

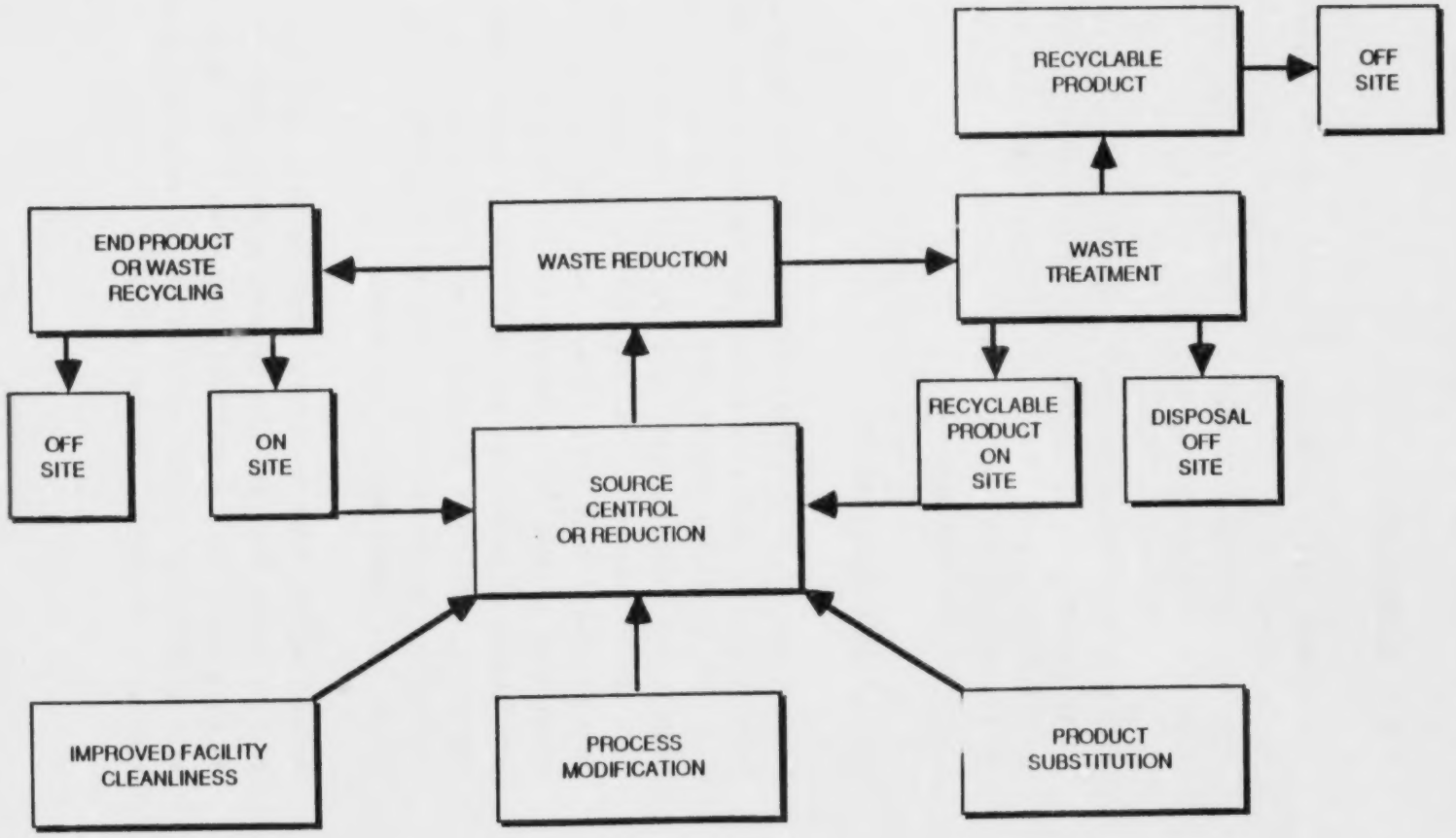
Figure 2.4-1 illustrates the components involved in any consideration of waste reduction. It was the goal of this grant to identify a treatment process or processes that could be easily applied to arsenic waste reduction in the Gallium-Arsenide microchip manufacturing process. As stated above, that goal has been achieved.

2.4.2 GENERAL DISCUSSION

Arsenic and arsenical compounds have been reported as waste products of the metallurgical industry, glassware and ceramic production, tannery operations, dye, and pesticide manufacturer. Other industrial sources include the organic and inorganic chemicals and petroleum refining industries, and the rare-earth industry. The manufacture of Paris green and calcium meta-arsenate, both insecticides, was reported to produce wastewaters containing arsenic[5]. Although arsenic is widely associated with the manufacture of herbicides and pesticides, a recent study concluded that the inorganic pesticides industry (including arsenic based compounds) is fading[6]. Arsenical wastes from these sources would be expected to assume less importance in that event.

Arsenic wastes from nonferrous smelting have been reported in the literature, although the main form appears to be as extremely small particles from which arsenic can be profitably recovered.[7,8] High arsenic levels have been encountered in raw municipal water supplies, necessitating arsenic removal by the water treatment industry.

FIGURE 2.4-1
WASTE REDUCTION COMPONENTS



Only limited information was encountered on current levels of arsenic in industrial wastes, and on current treatment processes and removals obtained[13,14]. Most recent industrial literature[6,15], while referring to arsenical wastes and to the severe pollution resulting from their discharge, presents no specific treatment processes or industrial waste values. More up-to-date information is available on the removal of arsenic from drinking water, and in fact the methods for arsenic treatment of both drinking water and industrial wastes are similar.[12] The treatment methods and arsenic removal efficiencies discussed in detail below are summarized in Table 2.4-1. No treatment costs directly related to wastewaters were encountered in this literature search.

Effluent arsenic levels of 0.05 mg/l are obtainable by use of precipitation of the arsenic as the sulfide, by addition of sodium or hydrogen sulfide at pH 6-7[13]. Polishing of the effluent by sand filtration would presumably be required to meet the quoted effluent level.

Two common water treatment methods have been found to be effective in arsenic removal, they are lime precipitation and carbon adsorption. The lime process was found to reduce an initial arsenic level of 0.2 mg/l down to approximately 0.03 mg/l. Absorption through a charcoal bed yielded an effluent containing 0.06 mg/l of arsenic.[29]

Arsenic reduction in a conventional water treatment plant employing coagulation, settling, and filtration has been reported[18]. Ferric sulfate employed as a coagulant, was able to reduce the arsenic content of the water from 25 mg/l down to 5 mg/l or less. Lund has suggested that the basis of this arsenic removal method is that arsenic is complexed with heavy metals and thereby removed when the heavy metal precipitates[5]. In the Buswell study described above[18], the arsenic would thus be complexed and removed by precipitation with the ferric hydroxide formed upon addition of the coagulant, ferric sulfate.

TABLE 2.4-1

SUMMARY OF ARSENIC TREATMENT METHODS AND REMOVALS ACHIEVED

Treatment	Initial Arsenic, mg/l	Final Arsenic, mg/l	Percent Removal	Reference
Lime Softening	0.2	0.03	85	16
Precipitation with Lime (plus Iron)	---	≤0.05	---	3
Charcoal Filtration	0.2	0.06	70	16
Ferric Sulfide Filter Bed	0.8	0.05	94	11
Coagulation with Ferric Sulfate	25.0	≤5	≥80	18
Coagulation with Ferric Chloride	3.0	0.05	98	20
Precipitation with Ferric Hydroxide	---	0.6	--	19
Precipitation with Ferric Hydroxide	362.0*	15-20*	94-96	4
Precipitation with Sulfide Salt	---	0.05	--	13

*as arsenious oxide

Viniegra and Marquez[10] have also employed ferric hydroxide to effectively remove arsenic from water supplies. Their treatment sequence involved addition of ferrous sulfate for precipitation, and subsequent filtration. Effluent arsenic levels less than 0.05 mg/l was the goal of the treatment process. Similar treatment of arsenic-contaminated water has been reported.[9,19]

Various standard treatment methods were evaluated for removal of arsenic with coagulation partially effective. Passage of the water through a ferrous sulfide filter bed, followed by addition of bone carbon, settling, and filtration reduced the level of arsenic from 0.8 to 0.05 mg/l. Passage through ferrous sulfide followed by settling and filtration through sand and coke reduced the concentration from 0.8 mg/l to "only a trace."[22] In a written discussion, Irukayama provided data on removal of arsenic by the use of ferric chloride coagulant[20]. Ferric chloride was added after adjustment of the water pH to 10.3 by slaked lime, $Ca(OH)_2$. Ferric hydroxide precipitate formed, and was removed by filtration.

Lund has reported that arsenic in an industrial waste which also contains heavy metals in solution can be concurrently removed with precipitation of the heavy metals. Approximately 90 percent reduction of arsenic is to be expected[16,23]. A patented waste recycle process[15] removes arsenic and cadmium simultaneous with the precipitation of iron as ferric hydroxide. This is based upon the same removal mechanism described by Lund for industrial wastes, and discussed in some detail above with respect to removal of arsenic from drinking water. Cherinskii and Ginzhurg[5] have also described the use of this technique in reducing an arsenic level of 362 mg/l (as arsenious oxide) to 15 20 mg/l. Ferrous sulfate and lime were added to the waste, which originated from a pesticide manufacturing process. Ferric hydroxide was removed by settling.

Arsenic removal from wastewaters from the rare-earth industry, Skripach, et al.[34] have reported that arsenic can be effectively removed by lime addition, but only in the presence of iron.[3] Similar experience was described by Nilsson[20], who was unable to achieve effluent arsenic levels below 9.7 mg/l through lime treatment of a low iron water.

Maruyama, et al.,[14] performed extensive pilot plant studies on physical-chemical removal processes for arsenic in municipal wastewater. This treatment process involved addition of a coagulant, followed by flocculation and settling, dual-media filtration, and carbon adsorption. Types and levels of coagulants employed are given in Table 2.4-2. Treatment results for an initial arsenic concentration of 5 mg/l are reported in Table 2.4-3. For this wastewater, filtration provided little or no improvement, although carbon column polishing was effective in all cases.

No costs directly bearing on arsenic removals from either drinking waters or waste waters were encountered in an extensive search of the literature. However, the most effective, and most commonly reported arsenic treatment process is one quite similar to that employed in treating drinking water. This is coagulation, sedimentation, and filtration. If the arsenic-bearing waste is acidic, pH adjustment to an alkaline condition may be required, and additional chemical costs are associated with that. Adjustment of pH is most frequently by use of lime, also employed in water treatment.

Arsenic is used as a raw material and produced as a waste in a variety of industrial processes. There appears to be extremely little information available in the current literature on industrial waste levels and on industrial waste treatment processes. Removal of arsenic from municipal waters has been more widely reported. Arsenic treatment processes for both municipal waters and industrial wastes seem to be similar and basically involve coagulation to produce a ferric hydroxide precipitate which can then be filtered. This process has consistently yielded effluent arsenic levels of 0.05 mg/l or less. The treatment processes employed all deal with soluble arsenic. In almost every case, filtration or other solid-liquid separation is required once the arsenic is in an insoluble form.

2.4.3 FILTRATION[31]

Suspended solids are separated from fluids via three mechanisms: inertial impaction, diffusional interception and direct interception as illustrated in Figure 2.4-2. Both inertial impaction and diffusional interception are

TABLE 2.4-2

TREATMENT SYSTEMS FOR ARSENIC REMOVAL[14]

System	Coagulant	pH
Iron	Ferric Sulfate @ 45 mg/l Fe	6.0
Low Lime	Lime @ 260 mg/l Ferric sulfate @ 20 mg/l Fe	10.0
High Lime	Lime @ 600 mg/l	11.5

TABLE 2.4-3

PILOT PLANT ARSENIC REMOVAL[14]

System	Cumulative Percent Removal			Effluent Concentration mg/l
	Settling	+ Filtration	+ Carbon	
Iron	90	89	96-98	0.06
Low Lime	79	79	82-84	0.92
High Lime	73	75	84-88	0.77

FIGURE 2.4-2
MECHANISMS OF FILTRATION

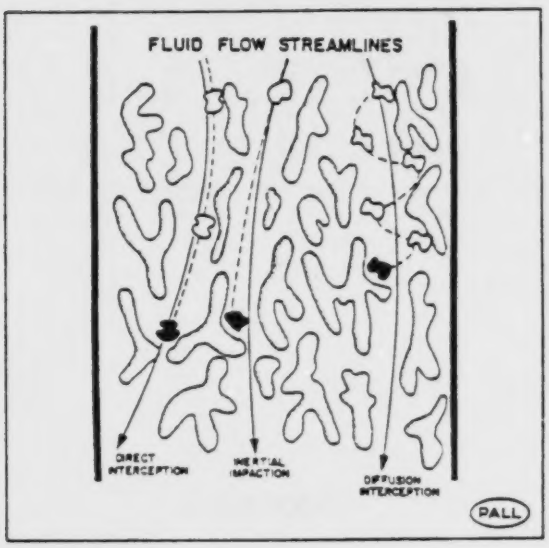
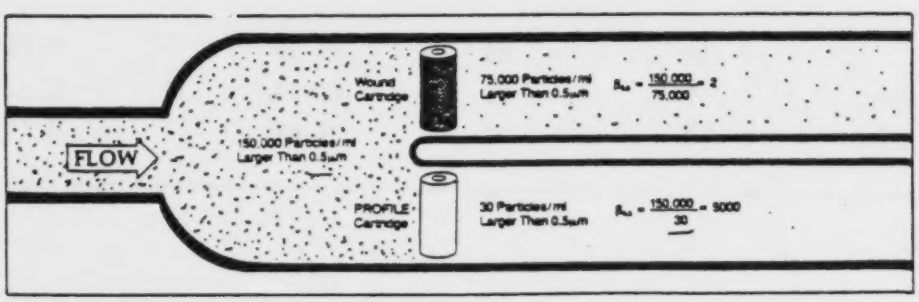


FIGURE 2.4-3
BETA VALUES IN USE



Reproduced from best available copy.

much less effective with liquids than with gases. Since the density of a particle will typically be closer to that of a liquid than to that of a gas, deviation of a suspended particle from the liquid flow line is much less, and this impaction on the structure of the medium is less likely. Diffusional interception in liquids occurs to only a very limited extent because Brownian Motion is not nearly as pronounced in liquid suspensions as in gaseous suspensions.

While inertial impaction and diffusional interception are not effective in liquid service, direct interception is equally as effective in both liquid and gas service and is the primary mechanism for separating particles from liquids. Direct interception is easily understood in the case of a woven wire mesh filter with uniform pores and no thickness or depth; once a particle passes through an opening, it proceeds unhindered downstream. Yet such a filter will collect a very significant proportion of particles whose diameter is smaller than the openings or pores of the medium. Several factors such as irregular particle shapes, bridging, and surface interactions help account for this collection.

Every type of filter will collect particles finer than its absolute rating, and under extreme impulse conditions such finer particles may release. Filters in which the structural portions of the medium are free to move in response to increased pressure are particularly prone to this occurrence, and they may even release downstream particles larger than their pore size.

In a well-designed filter, particles larger than the pore size do not pass downstream of the medium. The most successful approach to zero particle release is achieved by using a filter medium in which the pores will not enlarge under pressure and in which the thickness is sufficient so that in normal service substantially all the incident particles are collected in the first tenth to fifth of the thickness, leaving the rest available to stop undersize particles which may be released from the upper layer on impulse.

Aids to Liquid Filtration

It is possible to supplement the three principal mechanisms of filtration, and to enhance a filter's effectiveness in removing particles from a liquid. Several methods include electrostatic deposition, flocculation and filter aids.

Most particles carry a negative charge. It is possible therefore to enhance the particle capture mechanisms of a filter by inducing a desired charge (usually positive) on the filter. But, one must use great caution when seeking to aid the filtration of liquids through electrostatic deposition. These charges are often unstable and influenced by pH of the contacting fluid, time, and the deposition of charged particles.

Flocculation is one way to enhance filterability by causing fine particles to "clump" together to form larger particles that are easier to filter. Flocculation of particles by the addition of polyelectrolytes (long chain molecules with many positive and negatively charged ionic points along the chain length) to the fluid system is a common practice. Polyelectrolytes such as soluble starches, gelatin, and derivatives of polyacrylates attach themselves to many oppositely charged particles in the liquid causing their agglomeration and increasing their settling rate. They should be selected empirically for each fluid process. Whether or not a polyelectrolyte can be used in a filter process depends on its performance and cost.

The ease with which fine size particles can be removed from a liquid stream can also be increased by the addition to the suspension of small amounts of filter-aids. This is known as a "body feed" or "body aid", and should not be confused with precoat filtration where filter aid is first deposited on a filter and the suspension then caused to flow through.

Perhaps the most commonly used filter-aid is diatomaceous earth, which consists of the sedimentary deposits of fossilized diatoms. The diatom skeletons have a wide variety of shapes, and it is this property which

enables them to produce filter cakes of high permeability. Other filter-aids include perlite (an igneous rock formed by the quenching of molten volcanic lava in water), carbon, and cellulose.

Filter aid filtration is not common in fluid clarification but, when used, is often found upstream of cartridge filtration. Cartridge filters are used as "trap" filters downstream of precoat filters to capture any filter aid which may "bleed" past the filter medium.

Filter Types

In recent years it has become increasingly common to classify filters and filter media as either "depth type" or "surface type". Unfortunately, filter manufacturers have been unable to agree upon an "official" definition of the terms. As a result, much misunderstanding is encountered in the field on this subject. A better classification is whether the media is fixed or not fixed under changing pressure conditions.

Non-Fixed Random Pore Depth Type Media

Non-fixed random pore depth type media depend principally on the filtration mechanisms of inertial impaction and/or diffusional interception to trap particles within the interstices or spaces of their internal structure. Examples of this type of media are felts, woven yarns, asbestos pads, and packed fiberglass. These filters are, therefore, not usually used for liquid service.

Fixed

Fixed random pore depth type filters consist of either layers of medium or a single layer of medium having depth, depend heavily on the mechanism of direct interception and are so constructed that the structural portions of the medium can not distort.

Removal Ratings

Various rating systems have been evolved to describe the filtration capabilities of filter elements. Unfortunately, there is no generally accepted rating system and this tends to confuse the filter user. Several of the systems now in use are described below.

Nominal Rating

Many filter manufacturers rely on a Nominal Filter Rating which has been defined by the National Fluid Power Association (NFPA) as: "An arbitrary micron value assigned by the filter manufacturer, based upon removal of some percentage of all particles of a given size or larger. It is rarely well defined and not reproducible." In practice, a "contaminant" is introduced upstream of the filter element and subsequently the effluent flow (flow downstream of the filter) is analyzed microscopically. A given Nominal Rating of a filter means that 98% by weight of the contaminant above the specified size has been removed; 2% by weight of the contaminant has passed downstream.

Absolute Rating

The NFPA defines Absolute Rating as follows: "The diameter of the largest hard spherical particle that will pass through a filter under specified test conditions. It is an indication of the largest opening in the filter element. Such a rating can be assigned only to an integrally bonded medium (such as a fixed pore depth media or sintered metal media).

There are several recognized tests for establishing the Absolute Rating of a filter. What test is used will depend on the manufacturer, on the type of medium to be tested, or sometimes on the processing industry. In all cases the filters have been rated by a "challenge" system. A filter is challenged by pumping through it a suspension of a readily recognized contaminant (e.g. glass beads or a bacterial suspension), and both the influent and effluent examined for the presence of the test contaminant.

Beta Rating System

While absolute ratings are clearly more useful than nominal ratings, a more recent system for expressing filtration rating is the assignment of Beta Ratio values. Beta Ratios are determined using the Oklahoma State University, "OSU F-2 Filter Performance Test." The test, originally developed for use on hydraulic and lubricating oil filters, has been adapted for rapid semi-automated testing of filters for service with aqueous liquids, oils, or other fluids.

The rating system measures the total particle counts at several different particle sizes, in both the influent stream and effluent stream. A profile of removal efficiency emerges for any given filter. Figure 2.4-3 illustrates this principle.

Choosing the Proper Filter

Among the more important factors that must be taken into consideration when choosing a filter for a particular application are the size, shape, and hardness of the particles to be removed, the quantity of those particles, the nature and volume of fluid to be filtered, the rate at which the fluid flows, whether flow is steady, variable and/or intermittent, system pressure and whether the pressure is steady or variable, available differential pressure, compatibility of the medium with the fluid, fluid temperature, properties of the fluid, space available for particle collection, and the degree of filtration required.

Nature of Fluid

The materials from which the medium, the cartridge hardware, and the housing are constructed must be compatible with the fluid being filtered. Fluids can corrode the metal core of a filter cartridge or a pressure vessel, and the corrosion will in turn contaminate the fluid being filtered. Thus it is essential to determine whether a fluid is acid, alkali, aqueous, oil or solvent based, etc.

Flow Rate

Flow rate is dependent on two general parameters, pressure and resistance. Flow rate depends directly on pressure and inversely on resistance. All other factors being equal, if the pressure on a fluid is increased, then the flow rate of that fluid will increase.

Viscosity is the resistance of a fluid to the motion of its molecules among themselves or a measure of the thickness or ability to flow of a fluid. Water, ether, and alcohol have low viscosities; heavy oils and syrup have high viscosities. Viscosity affects resistance directly. If all other conditions remain constant, doubling the viscosity in a filter system gives twice the original resistance to flow. Consequently, as viscosity increases, the pressure required to maintain the same flow rate increases.

Temperature

The temperature at which filtration will occur can affect both the viscosity of the fluid, the corrosion rate of the housing, and filter medium compatibility. Viscous fluids generally become less viscous as temperature increases. Thus, it is important to determine the viscosity of a fluid at the temperature at which filtration will occur.

Pressure Drop

Everything a fluid passes through or by contributes resistance to the flow of that fluid in an additive fashion. The pressure losses due to flow of the fluid through the tubing, piping, etc., couples with the pressure loss through the filter to produce resistance.

Resistance to flow through a clean filter will be caused by the filter housing, cartridge hardware, and the filter medium. For a fluid of given viscosity, the smaller the diameter of the pores or passages in the medium, the greater the resistance to flow. When a fluid meets resistance in the form of a filter, the result is a drop in pressure downstream of that

filter, and the measurement of the pressure drop across the filter is called the differential pressure. Thus, for all practical purposes the terms pressure drop, differential pressure, are synonymous. The more resistance a filter medium offers to fluid flow, the greater the differential pressure at constant flow.

In the preceding discussion it was tacitly assumed that the fluid was completely free of particulate contamination. But in reality there will always be some particles present in a system. As the filter does its job, particles will be stopped by and partially occlude or block the pores or holes of the filter medium, thereby increasing resistance to flow.

In choosing a filter, therefore, one must provide for sufficient pressure source not only to overcome the resistance of the filter, but also to permit flow to continue at an acceptable rate as the medium plugs so as to use fully the effective dirt holding capacity of the filter. If the ratio of the initial clean pressure drop through the filter to total available pressure is disproportionally high, unacceptable flow will quickly result even though the medium's capacity for collecting dirt has not been exhausted. When this occurs, the proper solution is usually to increase pump capacity or gravity head, or as an alternative, to reduce clean pressure drop by increasing filter size.

Filter cartridges exhibit an exponentially increasing pressure drop vs. dirt capacity of the filter is mostly consumed before the sharp increase in pressure drop. Consequently, the available system pressure source should be at least sufficient to overcome the pressure drop so as to utilize most of the dirt holding capacity of the filter medium.

In choosing a pressure source, one must take into consideration the resistance to flow of the filter, both constant resistance components (filter housing and element hardware), and the variable resistance components (filter cake and medium). As filtration proceeds at constant flow, there will be an increase in pressure drop made up of a constant component and an increasing variable component. Eventually, the increasing pressure drop

component becomes so large as to either clog the filter and stop flow or to structurally damage the filter. Enough pressure drop should be available to satisfy both components at least to filter clogging.

Surface Area

The life of most screen and fixed pore depth type filters is greatly increased as their surface areas are increased; in fact, the ratio can be as much as the square of the area ratio. From the foregoing it is apparent that an increase in surface area will yield at least a proportional increase in service life. Under favorable circumstances, the ratio of service life may approach the square of the area ratio. In many, if not most cases, a filter user will save money in the long run by paying the higher initial cost of a larger filter assembly.

As the surface area is increased, a larger housing (container or pressure vessel) is required. There is, of course, a practical limit to housing size. It is for this reason that filter manufacturers use convoluted or pleated structures to provide large surface areas in small envelopes, thereby keeping housing size and cost to a minimum.

Void Volume

Void volume, or the open area of a medium, is always of great importance. All other factors being equal, the medium with the greatest void volume is most desirable because it will yield longest life and lowest initial clean pressure drop per unit thickness. As the fiber diameter decreases, the void volume increases, assuming constant pore size. Other factors, however, such as strength, compressibility as pressure is applied (which reduces void volume), compatibility of the medium with the fluid being filtered, cost of medium, cost of constructing that medium into a useable filter, etc., must all be considered when designing a filter for a particular application.

Degree of Filtration

The filter chosen for a given application must be able to remove contamination from the fluid stream to the degree required by the process involved. Once the size of the contaminants to be removed has been determined, it is possible to choose a filter with the particle removal characteristics needed. Choosing a filter with a pore size finer than required can be costly because the finer the filtration, the more rapid the clogging and the higher the cost.

One should select a medium which will not change its structure under system-produced stress because as system pressure rises to accommodate flow as filter cake builds, strands of woven wire mesh must not separate to produce a larger pore. When it is necessary to support thin, membrane-type filters, attention must be given to the characteristics of the support material chosen. Support materials can react with the fluid, add significant resistance to flow, and cause shorter filter life.

Prefiltration

The purpose of a prefilter is to reduce overall operating cost by extending the life of the final filter. Extending final filter life may not in itself be sufficient to justify prefiltration; overall cost reduction is usually the principal consideration. Most applications are better served by increasing final filter area rather than by providing a prefilter. This is because increasing final filter area always yields a longer cycle and lower operating costs. Doubling the area of the final filter will result in two to four times the life. This approach also results in lower costs, requires less labor input, and permits operation with less power at lower pressure drop. Cost is less because one housing is used instead of two, and cost is further reduced because the larger filter installation has life in service which is proportionally larger than the increase in area. Clean pressure drop is reduced because of larger area, whereas a prefilter always increases pressure drop. Power required is reduced because pressure drop through most of the filtration cycle is lower.

Selection of filtration equipment such as those illustrated in Figure 2.4-4 requires a great deal of specific process information. Such information as particle distribution of solids, the amount of solids, the wastestream flowrate, pH, temperature pressure etc. all impact proper filter design and specification. Figure 2.4-5 is an engineering figure used for selection of the filter type based on process information.

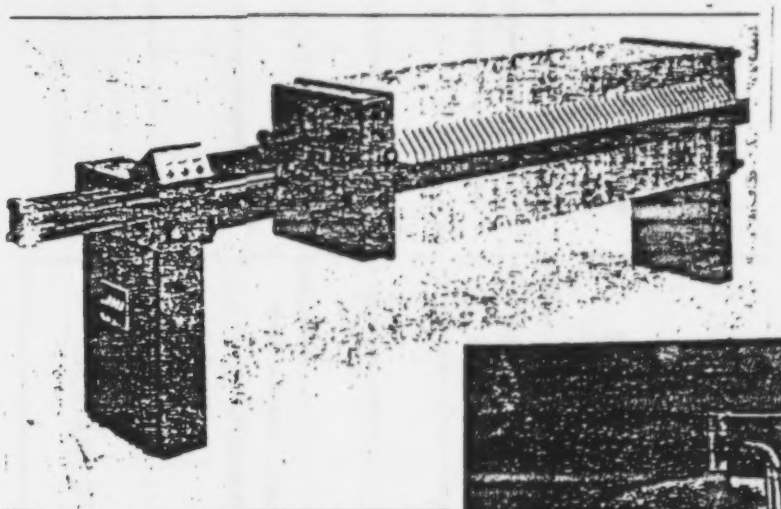
2.4.4 PRECIPITATION WITH SODIUM SULFIDE[25]

Sulfide precipitation is an effective process for the treatment of industrial wastes containing highly toxic heavy metals. The attractive features of the sulfide precipitation process are: attainment of high degree of metal removals over a broad pH range, effective precipitation of certain metals (such as: As, Cu, Cd, Hg) even at very low pH, low detention time requirement in the reaction tank because of the high reactivity of sulfides, and the feasibility of selective metal recovery. With sulfide precipitation, the high reactivity of sulfides with heavy metal ions and the very low solubilities of the heavy metal sulfides over a broad pH range are features not found with the hydroxide precipitation processes.

Industries engaged in metal finishing or metal production operations use large quantities of contact process water, and the spent process wastewater streams contain moderate to high concentrations of As, Cd, Cu, Zn, Pb, Hg, etc. Various physical-chemical treatment methods to remove heavy metals have been reported in the literature. Hydroxide (lime) precipitation of heavy metals followed by settling of the precipitates is most often used to treat industrial wastewaters. However, the minimum solubilities for different metals occur at different pH values and the hydroxide precipitates are amphoteric in nature and thus maximum removal efficiency of mixed metals cannot be achieved at a single pH.

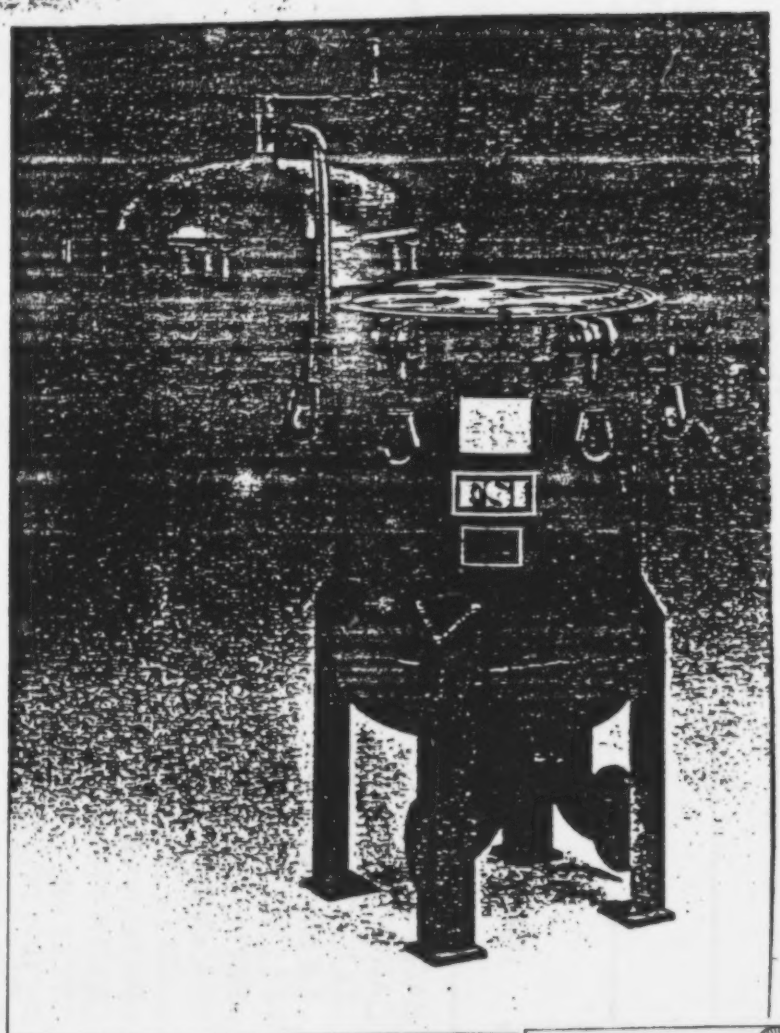
Sulfide precipitation (with Na_2S or NaHS) processes used to remove heavy metals have gained considerable importance. Arsenic separation behavior is particularly emphasized because of its importance to the microelectronics industry as well as the non-ferrous metal production industry.

FIGURE 2.4-4
FILTRATION EQUIPMENT



ilter presses are convenient for retrofit and expansion

Ultrafiltration cartridges used for critical applications

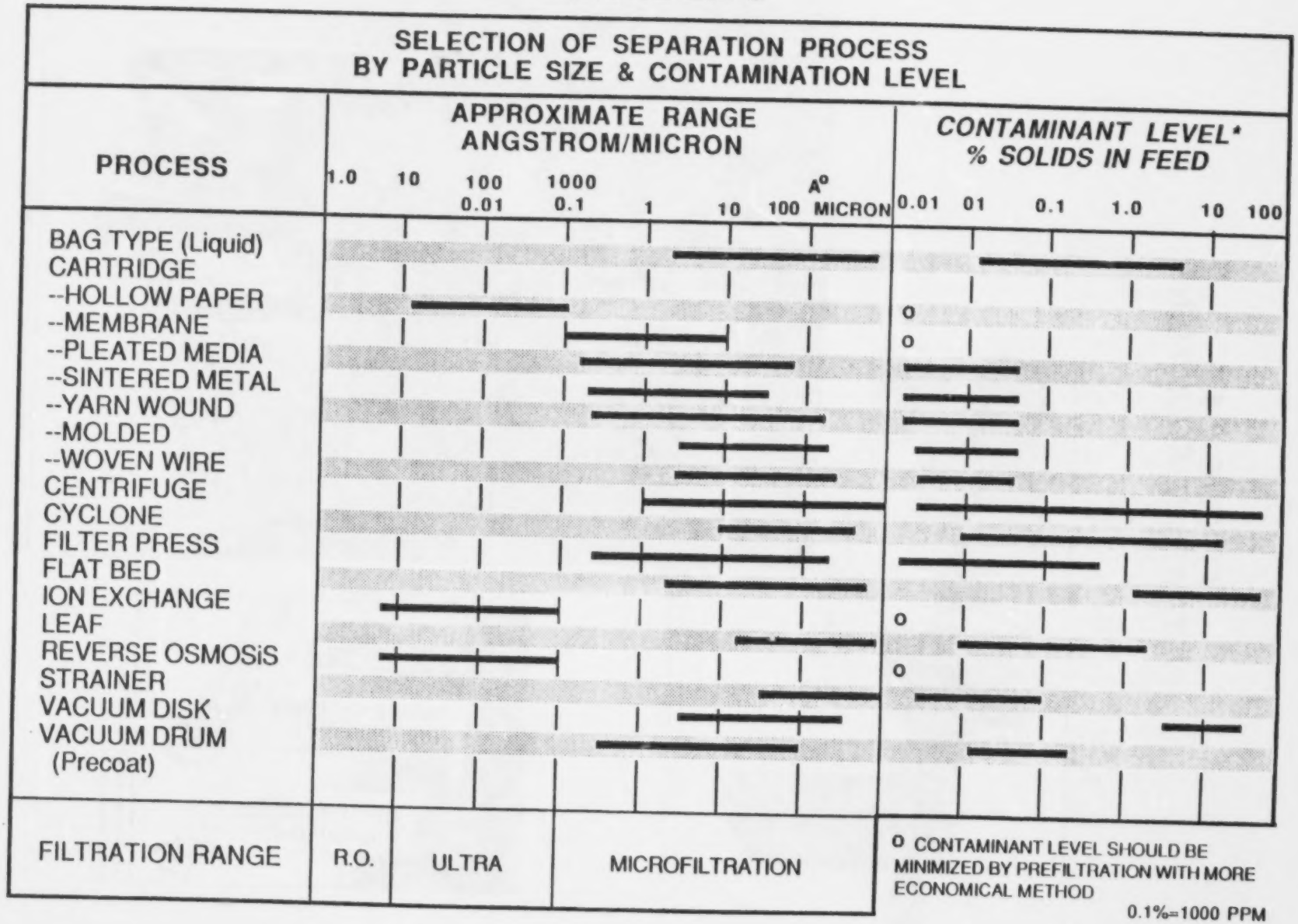


Improved fabric quality opens new applications for bag filters

Reproduced from best available copy.

FIGURE 2.4-5

SELECTION OF SEPARATION PROCESS BY PARTICLE SIZE & CONTAMINATION LEVEL



Sulfide Precipitation Reactions

Most heavy metal sulfides have very low solubilities, even at acidic pH values. HgS (AsS_3, CuS, CdS, and PbS can be completely precipitated even at pH 2. The extent of metal sulfide precipitation is a function of pH, type of metal, sulfide dosage, and other interfering ions that might be present. The primary reactions between As(III) and sulfide are listed in Table 2.4-4.

Arsenic precipitates only in acidic pH with the solubilities of other metals decreasing as pH increases. Metal hydroxide precipitate solubilities are considerably higher than the corresponding sulfide precipitates and the precipitation of hydroxide occurs only in a narrow pH range. With sulfide precipitation, a residual concentration less than 0.1 mg/l metal (for Cu, Cd, Pb, and Zn) could be achieved at $4 \leq pH \leq 12$.

A full-scale plant was put into operation in 1978 and was designed to precipitate (at pH 3-5) As, Zn, Cu, Pb, Cd, and Hg as sulfide at acidic pH for possible recovery of metals and to remove fluoride separately by lime (at pH < 10) as CaF_2 for landfill of Hewlett-Packard's arsenic were principle soluble, this process would be almost identified. A schematic diagram of the process is shown in Figure 2.4-6. The wastewater was first partially neutralized (to pH 2.5 - 3.0) with NaOH, and then Na_2S (as 15% Na_2S solution) was added and controlled by monitoring pH. The sulfide precipitate was removed by sedimentation (after polymer addition) and post-filtration. The wastewaters treated also contained fluoride, which was removed by precipitation with lime following sulfide precipitation.

Bench-scale sulfide precipitation experiments were conducted with three actual scrubber wastes (Table 2.4-5) obtained from a copper smelting operation. The wastes contained high concentrations of heavy metals, iron, and arsenic. Previous studies with actual smelter effluents have shown that high heavy metal removal efficiencies can be achieved by precipitation with sodium sulfide followed by separation of the sludge from the clarified wastewater. Arsenic removal was dependent on the wastewater

TABLE 2.4-4

ARSENIC (III) - SULFIDE PRECIPITATION REACTIONS

Reactions
$As_2S_3\ (s) + 4\ H_2O \rightleftharpoons 2HAsO_2 + 3\ H_2S$
$HAsO_2 \rightleftharpoons H^+ + AsO_2^-$
$2\ As_2S_3\ (s) + 2H_2O \rightleftharpoons 3\ H^+ + As_3S_6^{3-} + HA_sO_2$
$As_2S_3\ (s) + S^{2-} \rightleftharpoons AsS_2^-$
$AsS_2^- + H^+ \rightleftharpoons H_2S_2$
$H^+ + S^{2-} \rightleftharpoons HS^-$
$H^+ + HS^- \rightleftharpoons H_2S$

TABLE 2.4-5

ANALYSIS OF ACTUAL SCRUBBER BLOWDOWN WATERS

Parameter	Concentration		
	Batch I	Batch II	Batch III
pH	1.65	1.80	2.80
As	100 mg/l	307 mg/l	612 mg/l
Se	3.0 mg/l	2.8 mg/l	1.5 mg/l
Cd	10.5 mg/l	12.0 mg/l	15.0 mg/l
Zn	86 mg/l	202 mg/l	175 mg/l
Cu	297 mg/l	792 mg/l	1600 mg/l
Fe	149 mg/l	441 mg/l	122 mg/l
Pb*	39 mg/l	142 mg/l	62 mg/l
Hg	2.0 mg/l	1.5 mg/l	-
SO_4	700 mg/l	1300 mg/l	2700 mg/l

*91% of Pb is present as insoluble lead (Pb SO_4).

characteristics. Since arsenic precipitates only at low pH values this study was directed to establish the possibility of simultaneous removal of arsenic (by adsorption on precipitates or by Fe-As interaction) and heavy metals at alkaline pH values with Na_2S dosage $\leq$ 1.0x.

Sulfide precipitation experiments with the three scrubber wastes (Table 2.4-5) were conducted after initial pH elevation (with lime slurry) to 5.0 - 6.0. The sulfide precipitation reaction pH was varied between 7.5 - 8.5. The metal separations obtained with Batch I and Batch II wastes were quite similar; but with Batch III waste the arsenic separation was considerably poorer than the results obtained with Batch I or Batch II wastes. For both Batch I and Batch II wastes 98-99.6% metal (including As) removals were obtained at 0.6X dosage and pH 8.0. With Batch III waste, variable sulfide dosage studies again indicated 0.6X to be optimum dosage, but arsenic removal was only 83%.

Studies showed that the value of the molar ratio of Fe/As in the raw waste determined the extent of arsenic separation. In an effort to understand the effect of Fe^{+3} on arsenic separation, several experiments were conducted with normal wastes without Fe^{+3}.

The results in Table 2.4-6 show that arsenic removal dropped considerably in the absence of Fe^{+3}. With less than theoretical sulfide dosage, Fe^{+3} is precipitated as $Fe(OH)_3$ and thus enhances arsenic removal. The decrease in Fe/As ratio from 2.01 to zero caused arsenic separation to drop from 98% to 59%. The molar ratio of Fe/As for both Batch I and Batch II wastes were about 2.0 and arsenic removal was excellent. The Batch III waste had a molar Fe/As ratio of 2.7 and arsenic separation was only 82%. By increasing the Fe/As ratio of Batch III waste to 1.0, arsenic separation increased to 99% (Figure 2.4-7). Figure 2.4-7 shows that arsenic removal is reduced at molar Fe/As less than 0.8. A different type of actual copper plant waste containing arsenic, other heavy metals gave greater than 99% removal of all heavy metals (except arsenic) at the optimum sulfide dosage. The arsenic separation with this waste was only 40% because of the low molar Fe/As ratio (0.13).

TABLE 2.4-6

EFFECT OF IRON/ARSENIC RATIO ON ARSENIC
AND HEAVY METAL SEPARATION

Waste	Molar $\frac{Fe}{As}$	Removal %				
		As	Cd	Zn	Cu	Pb
Synthetic Batch I type waste	2.01	98.5	99.0	98.6	99.9	99.9
Synthetic Batch I type waste without Fe^{+3}	0	59.0	99.0	99.3	99.9	99.0

TABLE 2.4-7

ANALYSIS OF INLET WASTEWATERS
(FULL-SCALE PLANT)

Parameter	Concentration, mg/l
pH	1.9 - 2.8
As	130 - 450
Zn	30 - 60
Pb	20 - 40
Cd	3 - 16
Cu	3 - 5
Hg	2 - 4
Fe	5 - 20
Sulfite (dissolved SO_2)	600 - 1000
SO_4	1500 - 2000
Fluoride (F)	90 - 130

FIGURE 2.4-6
SULFIDE PRECIPITATION PLANT
(BOLIDEN METALL, SWEDEN)

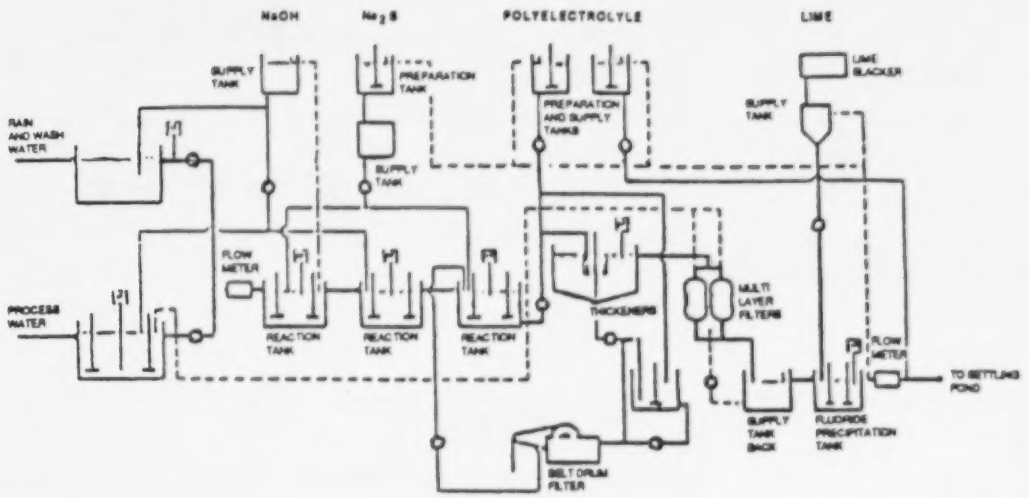
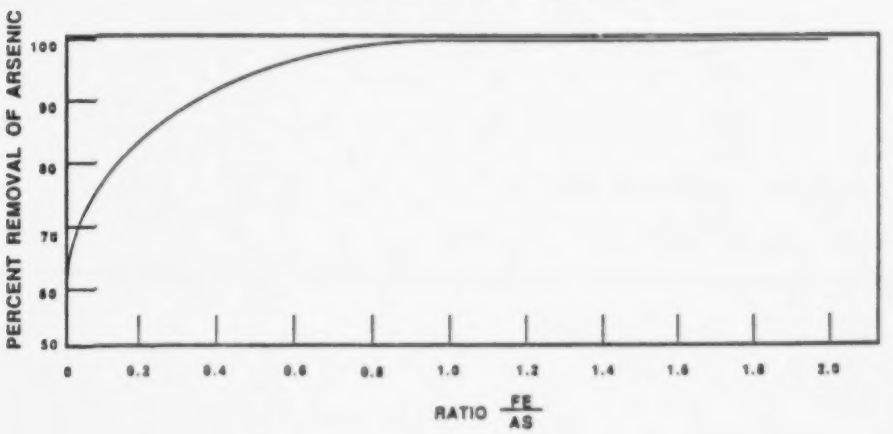


FIGURE 2.4-7
EFFECT OF RATIO OF FE/AS ON ARSENIC REMOVAL BY A COMBINATION HYDROXIDE-SULFIDE PRECIPITATION



Ideally, the separation of metals can also be achieved at acidic pH values since metal-sulfide precipitation reactions predominate over H_2S formation reactions. However, sulfide addition rates must be constantly controlled or H_2S gas would evolve. If wastewaters contain both heavy metals and fluoride, a two-stage precipitation (sulfide to precipitate heavy metals and lime to precipitate fluoride) process would be required to precipitate heavy metals (plus arsenic) and fluoride separately. Since the Boliden plant wastewater contained heavy metals, arsenic, and fluoride, two separate precipitation steps were utilized. The wastewater at the Boliden plant also contained high concentration of dissolved SO_2 (sulfite).

The major constituents of the inlet wastewater from copper and lead smelting operation were arsenic and zinc with copper, lead, mercury, and selenium present in smaller amounts. For the five full-scale test runs the combined process water and wash water inlet concentration ranges are shown in Table 2.4-7. The sulfide precipitation pH was in the range of 3.7 to 4.8 and the fluoride precipitation pH was in the range of 11.2 to 11.5.

Since arsenic precipitates best around pH 3 and zinc precipitation is complete above pH 5, two-step precipitation would be most desirable. The overall removal of all metals were excellent with sulfide precipitation followed by lime precipitation. (The ranges of removal of metals by sulfide precipitation only and by sulfide-lime combination process are shown in Table 2.4-8 for the five full-scale test).

The inadequate separations (by sulfide precipitation only) of As and Zn obtained in the full-scale tests were due to the wide fluctuations of pH and sulfide dosage and the consumption of a portion of the Na_2S reagent by dissolved SO_2 (sulfite) present in the wastewater. The control technique of sulfide dosage by pH rise was found to be insufficient for simultaneous arsenic and zinc removal at optimal efficiency. In order to understand the importance of sulfite-sulfide side reaction at acidic pH values, bench-scale studies were conducted with single metal salts in the presence of sulfite at acidic pH values. Depending on the metals studied part of the Na_2S was consumed by SO_3^{2-} to form elemental sulfur and thiosulfate. Even with

TABLE 2.4-8

REMOVAL OF METALS BY SULFIDE PRECIPITATION AND BY
SULFIDE PRECIPITATION FOLLOWED BY LIME PRECIPITATION
(FULL-SCALE PROCESS)

Component	Sulfide Precipitation	Sulfide + Lime Precipitation
As	67 - 87	96 - 99
Zn	51 - 75	99
Pb	97 - 99	97 - 99
Cd	99	99
Cu	>90	>90
Hg	99	99
Fe	2 - 26	>99
Fluoride	0	70 - 78

sulfide overdoses at low pH values no H_2S gas loss from the solutions occurred (also observed in full-scale tests) due to SO_3^{2-} - H_2S reactions. At stoichiometric Na_2S dosages (to form As_2S_3, ZnS, etc.) the sulfite-sulfide reaction played an important role only during precipitation of As and Zn at low pH values. The effects of sulfide-sulfite reaction were found to be negligible above pH 5.

In summary, the feasibility of a combination of hydroxide-sulfide precipitation (at pH 8-9) process, and a process involving sulfide precipitation (at pH 3-5) followed by lime precipitation, is established to achieve a high degree of separation of heavy metals and arsenic. The combination hydroxide-sulfide process required only 60% of the theoretical Na_2S dosage to provide effective separations of heavy metals and arsenic. Simple sulfide precipitation at pH 3-4 also provided excellent removals for Cu, Cd, Hg, and Pb. For precipitation of arsenic and zinc sulfide at pH < 5, the side reaction between sulfite (if present in wastewater) and sulfide must be considered. Hydrogen sulfide gas formation was never found to be a problem during precipitation because of the high reactivity of sulfides and heavy metals.

2.4.5 SOLIDIFICATION[26]

Many processes have been developed for waste treatment with most aimed at a specific waste stream with known chemical characteristics. The extruder-evaporator system was developed because of the need for a process to handle a variety of chemical properties associated with the relatively low-volume, highly-toxic wastes such as; arsenic, heavy metals or electroplating type wastes.

This solidification system is a simple mechanical process where the extruder-evaporator evaporates all unwanted solvent from the waste while homogenizing the waste constituents with a liquid plastic binder for discharge into a container. Once this waste-plastic mix has cooled, a significant volume reduction effect is realized. In addition to this, the system returns the clean solvent to the plant for reuse, thereby reducing plant makeup requirements. The end product is finely dispersed waste salts in a solidified plastic matrix.

This specific system will produce a solidified product with the hazardous constituents, regardless of their chemical characteristics, immobilized in a plastic binder. The flexibility and capability of this system to handle a wide variety of liquid and dry waste feed streams, in conjunction with most plastic binders (asphalt, polyethylene, polypropylene, urea formaldehyde and vinyl polyesters), means that industry has an effective solidification technology available for the treatment of their wastes. In addition to having this flexibility, the extruder-evaporator system will reduce the total volume of wastes produced, thus reducing ultimate disposal costs.

A large number of extruder-evaporators is operating worldwide in the chemical, plastics, food and nuclear industries and in hazardous waste stabilization and solidification applications. Operating experiences indicate minimal routine maintenance is required and minimal exposure of personnel to hazardous conditions during operation or maintenance.

This system, when incorporated into an actual processing plant, will provide the following advantages:

- Removal and recycle of unwanted solvent in the waste, and subsequent stabilization and solidification of the hazardous constituents.

- Volume reduction of the end product (up to 80% reduction), thereby reducing disposal requirements.

- Processing capability for handling the wide variety of wastes and allowing feeds from many different sources while maintaining adequate solidification.

- A number of binders may be used to meet the needs of the varying chemical characteristics of waste streams.

- The extruder-evaporator demonstrates ease of operation as it evaporates solvents, and disperses the remaining waste solids into a plastic matrix in a single step. The end product solidifies upon cooling.

- Utilization of batch or continuous modes of operation, thus reducing downtime, maintenance requirements and operator attention.

- Low operating costs due to reduced waste volume and weight shipped offsite, and low material costs for binder.

- The extruder-evaporator has been proven to be reliable in plastics compounding and hazardous waste processing applications.

- Dust-free operation at near ambient pressure, thereby eliminating the potential for in-process accidents, leaks and spills.

The extruder-evaporator is the major component of the solidification system. However, the complete system is designed to include collection and feed systems, processing, discharge and containment, container handling systems and remote control instrumentation. The system description that follows will reference an asphalt system, as this is the most widely used binder. However, use of other plastic binders would be comparable.

Feed System (General)

Many types of wastes (slurries, evaporator concentrates, ion exchange resins, chemical drains, sludges, manufacturing residues, incinerator ash, etc.) are handled by separate mixing and pretreatment components. The mixed wastes are then metered into the inlet barrel of the extruder-evaporator along with a controlled flowrate of plastic binder. The ratio of binder-to-waste is predetermined to maintain an end product of 50% waste salts and 50% asphalt, by weight.

Binder Feed (Asphalt)

An asphalt storage tank is located in an easily accessible area, near the solidification system and truck delivery access. The tank is sized to accommodate a bulk truck shipment of hot liquid asphalt to optimize delivery, storage and operational requirements. The hot asphalt remains in a liquid state by maintaining its temperature during storage above 250°F.

The asphalt feed system including transfer and metering pumps, strainers, heat tracing and instruments and controls is designed for operation from a main control panel.

Wastes

The solidification system includes a separate feed handling, conveying and metering system for each type of waste. Each feed system includes the required tanks, mixers, transfer pumps, metering pumps, feed conveyors, piping, valving, instruments and controls. These feed systems are interlocked to prevent wastes from being fed to the unit without the extruder-evaporator screws turning, containers in place, or asphalt flowing.

Processing

The processing operations (volume reduction and mixing) are accomplished in a motor-driven twin-screw extruder-evaporator. Twin co-rotating screws are utilized to mix and convey the waste product and immobilizing agent along the length of the machine. The housings or barrel sections in which the screws rotate are heated to evaporate free and entrained solvent from the mixture. The solvent removed from the feedstream is condensed in the steam (vent) domes, and recycled to the plant.

The asphalt and waste are fed to the extruder-evaporator in the first barrel, with the waste slightly downstream of the asphalt. The waste salts and the asphalts are kneaded into a homogeneous mix with asphalt. Entrained liquid is evaporated up through the subsequent steam domes and recycled back to the plant. The homogeneous mix of asphalt and waste is then discharged into a container for disposal.

OPERATING EXPERIENCE

The extruder-evaporator system is said to be one of the most extensively researched liquid waste solidification processes. European users claim the asphalt stabilization and solidification process is superior to the process

previously used (cement, cement silicate mixes, and urea formaldehyde) for a variety of reasons, i.e., volume reduction, cost savings, compatibility with waste feeds, superior end product, etc. Application of this system to the fixation and encapsulation of arsenic-laden wastes was tested by JBF Scientific, Wilmington, Massachusetts, under Contract No. 68-03-2503 from the U.S. EPA. Analysis results showed that there are great differences existing among the various processes. In general, the asphalt stabilized, and solidified samples showed a leach rate approximately two orders of magnitude below that of the next best method. Preliminary results of this study were presented at the Hazardous Waste Land Disposal Symposium in San Antonio, Texas on March 8, 1978.

2.4.6 ION EXCHANGE[32]

Packed beds of anion exchange resins in the chloride form may be utilized for selective removal of heavy metal contaminants from water. Using nitrate removal as an example, the exchange reaction of interest is:

$$RCL + NO_3^- \rightarrow RNO_3 + CL^-$$

where R denotes the resin phase. The reaction is reversed and the resin regenerated using a concentrated (typically 12 percent) solution of NaCl. The usual operational sequence is exhaustion, backwash, regeneration, displacement rinse and fast rinse. Typical package-type (50-200 gpm) ion-exchange resin beds are 3 to 6 ft. deep by 2 to 5 ft. diameter and contain 20 x 50 mesh resin beads. Typical exhaustion flow rates are 1-5 gpm/cu ft. Regeneration flow rates are much lower at 0.25-0.50 gpm/cu ft. with a minimum regenerant contact time of 45 minutes.

The length of a run to nitrate, arsenic or selenium breakthrough is determined mainly by the concentration of competing ions in the feedwater and the resin's preference for the contaminant ion compared to the other ions present. The higher the level of competing anions the shorter the ion exchange run; and the higher the resin preference for the contaminant ion

the longer the run. In the treatment pH range of 6.5 to 8.5 the commercially-available strong-base anion exchange resins prefer the ions of interest in the following order in dilute waters, i.e., less than approximately 700 ppm TDS.

$$SO_4 > SeO_4 > SeO_3 > HAsO_4 > NO_3 > HSeO_3\ Cl > HCO_3,\ H_2AsO_4 > F >> H_3AsO_3$$

The feedwater ions have been separated into zones which move at different velocities in a constant or proportional pattern toward the column outlet. The preferred species move at a slower rate through the column than do the nonpreferred species. The concentration velocity of any species is a function of the bulk fluid velocity and the slope of its equilibrium isotherm.

In our nitrate example, when the nitrate zone reaches the column outlet, an abrupt increase in nitrate is observed in the effluent and the run is terminated. An important fact to consider in ion exchange equipment design is that all species except the one most preferred will have effluent concentrations greater than influent concentrations after breakthrough. From the selectivity sequence shown above it is evident that all the inorganic contaminants are less preferred than the ubiquitous sulfate ion and, therefore, may be concentrated in the product water in this manner. Thus, the breakthrough point must be anticipated and not exceeded.

Ion exchange resin selectivity considerations

At least 40 different anion exchange resins are commercially available for single-bed or two-bed (strong-acid cation/weak-base anion) system designs. Many of these resins have been evaluated on a lab scale or on a pilot scale for nitrate removal applications. The EPA is carrying on continuing in-house and other research to determine the best resins for removal of all the inorganic contaminants amenable to ion exchange.

Although the previously given selectivity sequence is generally applicable to all the commercially available anion-exchange resins, the design engineer

has some control over the magnitude of the various preferences (separation factors) of one ion over another. For example, Clifford has shown that resins with closely-spaced exchange sites can have enormous preferences for divalent compared to monovalent ions. It has been pointed out, however, that these enormous divalent preferences don't translate into easily grasped, common-sense rules regarding column performance. For example, given the usual resin preferences for sulfate over nitrate, resins with the highest sulfate selectivities may actually be preferred in nitrate removal applications.

Regeneration considerations in ion exchange

In the usual ion exchange processes like water softening, countercurrent flow regeneration is more efficient than cocurrent regeneration. This is primarily due to "leakage" considerations which may not apply in contaminant removal processes for drinking water. For example, in nitrate removal, a leakage of 1-2 mg/l of NO_3-N may be quite acceptable since the MCL is 10 mg/l NO_3-N. On the other hand, excessive nitrate leakage, e.g., 5-10 mg/l NO_3-N, is undesirable because it substantially reduces the amount of raw water which may be bypass-blended with the treated water. It is a challenging engineering problem to minimize the product water cost by optimizing the ion exchange system design and operating conditions.

In some cases, the additional equipment complexities required for countercurrent regeneration may be justified but in many situations they probably won't be. Other possibilities to be examined to reduce operating costs are use of high exhaustion flow rates (>5 gpm/cu ft), reuse of spent regenerants, use of different regenerant concentrations and use of different regenerants (e.g., HCl, H_2SO_4, NH_4OH, NaOH). The use of various regenerants is especially relevant where regenerant disposal is a problem and more complex, two-bed, strong-acid/weak-base, ion-exchange systems are required. The common means of spent-regenerant disposal (for ion exchange and alumina adsorption) are sanitary sewer, stream dilution, deep-well injection, evaporation and dispersion in the ocean. Clearly, the first two alternatives will be unacceptable in most contaminant removal applications.

Ultimate disposal of salty, toxic regenerant solutions remains a major problem for single contaminant removal processes. It is somewhat less of a problem for the desalting process brines since regenerants are not used. However, the volumes to be disposed of from the desalting processes (20-50 percent of product flow) are substantially greater than those for the single contaminant removal processes (4-10 percent of product flow).

Ion exchange resins should be considered for arsenic removal but only if the flow stream, arsenic species and variations in pH are absolutely known. For wastewater systems with highly varying conditions, an arsenic removal system able to handle these non-steady state conditions should be considered.

2.4.7 ADSORPTION BY ACTIVATED CARBON[27, 32]

Batch studies were performed for a total of 15 different types of activated carbons to determine As(V) removal at various pH values by powdered and granular activated carbons. Most of the Darco carbons showed significant As(V) removal capacity while Nuchar and Filtrasorb brands exhibited little in comparison. Generally, powdered activated carbons had better capacity than granular activated carbon in arsenic removal. Tables 2.4-9 and 2.4-10 give comparisons of adsorption capacity at an optimum pH value of 4 by powdered and granular activated carbons, respectively. The activated carbon D-X demonstrates much better arsenic removal than the other carbons. Among granular carbons, type D-XI is the most effective adsorbent. Both the D-X and D-XI activated carbons were selected for further adsorption studies.

It is also found that the removal of As(V) species by activated carbons is markedly affected by the pH value. This can be attributed to the fact that the concentration distribution of arsenic(V) species and the development of surface charge on the activated carbon are pH-dependent phenomena. As the system pH changes, the speciation of arsenic(V) and the carbon surface charge vary. $H_2AsO_4^-$ and $HAsO_4^{2-}$ are the predominant species in the pH range studies (3 to 11).

TABLE 2.4-9
COMPARISON OF ADSORPTION CAPACITY BY VARIOUS TYPES OF POWDERED ACTIVATED CARBONS

CARBON	% As(V) REMOVED
D-XI	84.0
D-VIII	29.0
D-VII	22.0
D-VI	11.0
D-IX	11.0
N-I	10.0
N-II	5.0

BATCH EXPERIMENT CONDITIONS:

SODIUM ARSENATE (Na_2HAsO_4) $5X10^{-5}$ M
CARBON DOSE 1 g/L
pH=4.0
IONIC STRENGTH I-0.01 M $NaClO_4$
REACTION TIME-24 HOURS

TABLE 2.4-10
COMPARISON OF ADSORPTION CAPACITY BY VARIOUS TYPES OF GRANULAR ACTIVATED CARBON

CARBON	% As(V) REMOVED
D-X	61.0
N-V	15.0
N-IV	13.0
N-III	12.0
F-XII	13.0
F-XIII	7.0
F-XIV	11.0
F-XV	12.0

BATCH EXPERIMENT CONDITION:

SODIUM ARSENATE (Na_2HAsO_4) 10^{-4} M
CARBON DOSE 5 g/L
pH=4.0
IONIC STRENGTH I=0.01 M $NaClO_4$
REACTION TIME-24 HOURS

The results indicate that the amount of arsenate removed increases with pH to a maximum value at pH near 4.5, then decreases steadily as the pH increases to the basic range. This is similar to the adsorption of arsenate on aluminum hydroxide and phosphate and silicate on hydrous alumina where a maximum adsorption occurs at a specific pH value then adsorption density decreases with further pH change.

Steenburg first used the uptake of inorganic acid and base and the oxidation process to classify activated carbons into "H" and "L" types. Frumkin and Kruyt stated that the activation of carbon at 1000°C either in pure carbon dioxide (CO_2) or under vacuum, followed by exposure to oxygen at room temperature, results in a hydrophobic carbon surface capable of raising the pH of the solution, which has positive electrophoretic mobility. This type of carbon is what Steenburg called "L" type. By contrast, the oxidation of carbon by exposure to gaseous oxygen at temperatures between 200° and 400°C produces a carbon surface which is able to lower the pH of a solution, is hydrophilic, and has a negative zeta potential. This is a so-called "H" type. The hydrous activated carbon develops its surface charge according to the activity of potential-determining ions (OH^- and H_3O^+). A pH value of 7.5 was the zero point of charge. Between pH 3 and 7, which is also the main region of As(V) removal, $H_2AsO_4^-$ is the predominant species. Between pH 7 and 11 where $HAsO_4^{2-}$ is the major As(V) species, significant amounts of As(V) are still adsorbed although not as significant as in the lower pH region. This implies that specific adsorption is the major removal mechanism in addition to electrostatic attraction of the anion.

"H" type carbons, like the Darco Series, exhibit a significant adsorbing capacity for As(V). In contrast, adsorption of As(V) species by the "L" type activated carbons (such as the Nuchar Series) was poor, probably because of the electrostatic repulsion between anionic As(V) species and the negatively charged carbon surface over the pH range studied.

Interferences in Adsorption

Iron can drastically enhance As(V) removal by Carbon D-XI. Co-precipitation of iron with arsenate on the carbon surface may play an important role in As(V) removal.

Because the activated carbons that effectively remove As(V) such as D-XIII, D-X and D-XI contain significant amounts of ash that may not be amenable to base wash, it has been speculated that the removal of arsenic by these carbons might have some connection with the carbon ash. These carbon ashes were analyzed for moisture, ash content, silicate, calcium, magnesium, iron, aluminum, and phosphate, which are thought to be important to As(V) removal. To find out if silicate has any effect on As(V) removal, a suitable amount of silicate was mixed with As(V) solution in the absence of activated carbon. The results, however, show no As(V) removal by silicate.

Reactivation of Carbon

The low adsorption density of As(V) by carbon type D-X and D-XI at both ends of the pH scale suggests that arsenic-laden activated carbon can be desorbed by either a strong acid or a strong base. Kinetic data indicates that chemical regeneration is able to desorb As(V) from the carbon surface. However, reuse of the acid-base treated carbon was not successful. The results indicate that the adsorption capacity of carbon D-X was reduced dramatically after regeneration. One possible explanation is that strong acid and thermal treatment destroy the As(V) adsorption sites.

SUMMARY

The removal of As(V) from water by carbon adsorption is determined by pH, carbon type, and total As(V) concentration. Of the 15 different brands of commercial activated carbons tested, two activated carbons, D-X and D-XI seemed to be the most effective. Maximum As(V) removal occurred at pH 4 to 5. Electrostatic attraction and the formation of specific chemical bonds were the major adsorption mechanisms. This was evident from the reversal of surface charge on As(V) adsorption. Treatment with these activated carbons met drinking water standards (0.01 mg/L).

The presence of organics such as Tiron has no effect on As(V) removal, but the presence of Fe(II) drastically increased both the rate and the extent of As(V) removal.

Treating As(V) laden activated carbon with strong acid or strong base effectively stripped off adsorbed As(V) species from activated carbon surface. However as(V) adsorption was not restored by strong acid or base treatment. The As(V) adsorption capacity of the strong acid or base treated activated carbon was greatly improved by further treatment with Fe(II) salts. Fe(III), Ca(II), AL(III), and Mg(II) salts did little to enhance As(V) readsorption capacity, however.

2.4.8 ADSORPTION BY ACTIVATED ALUMINA, BAUXITE, AND CARBON[28,32]

Little is known about the adsorption mechanism of arsenic species on activated alumina, bauxite, and carbon. The mechanism relating to the adsorption of arsenate and arsenite ions on amorphous iron hydroxide and aluminum hydroxide was first studied by Ferguson and Anderson. The general conclusion was that the arsenic adsorption mechanism cannot be solely explained in terms of molecule-surface interaction, electrostatic interaction, or occlusion. The reported zero point of charge values for activated alumina and bauxite are slightly basic.

For As(V), $H_2AsO_4^-$ is the predominant species in the pH range between 3 and 6.5. It is apparent that $H_2AsO_4^-$ is the major species removed by activated carbon. It would not be surprising if this is a result of the reaction of the monovalent species with the oxo-function groups on the carbon surface as suggested by Huang and Wu. There is probably little affinity between carbon surface and the nonionic, divalent and trivalent forms of As(V). For As(III), H_3AsO_3 is the predominant species in the pH range from 0 to 9. For As(V) adsorption, negatively charged molecules were removed effectively onto the slightly positive or neutral charge surfaces. For As(III) adsorption, neutral H_3AsO_3 molecules were removed on relatively neutral charged surfaces (could be slightly positive or negative).

Adsorption Study

The three types of activated solids chosen for this study are: 1) 28 X 48 mesh, granular, Activated Alumina; 2) 30 X 60 mesh, granular, Activated Bauxite; 3) 8 X 30 mesh, Activated Carbon.

These three adsorbents were not subjected to any additional pretreatment prior to the adsorption study. Experiments were carried out with freshwater, seawater diluted ten times, seawater, and a 0.67 M sodium chloride solution. Trace metals from sodium chloride and seawater were coprecipitated with ferric hydroxide at pH 7.5. These solids were removed by a vacuum filtration technique through an 0.05μ membrane filter. In some cases sodium meta-silcate was added to the freshwater and seawater to evaluate the effect of soluble silicate on the adsorption of arsenic. There is evidence from the analysis of many water samples that both As(III) and As(V) are present under oxidizing as well as mildly reducing conditions.

As(V) concentrations in geothermal fluids range between 4 and 90 percent of the total soluble arsenic. In general, average As(V) concentrations lie between 10 and 40 percent of the total soluble arsenic. Under the mildly reducing conditions encountered in most geothermal reservoirs, thermodynamic calculations indicate that arsenic should be present as As(III). Sergeyeva and Khodskovsky concluded that the most probable form in which arsenic exists in hydrothermal solution (under mildly reducing conditions) is arsenious acid. The existence of both As(III) and As(V) species under these conditions may be a result of incomplete reduction of arsenate to arsenite. The kinetics of arsenate reduction to arsenite are unknown.

The existence of both As(III) and As(V) forms in surface waters is probably caused by the slow rate of oxygenation of arsenite to arsenate or bacterial reduction of arsenate to arsenite at neutral pH in localized areas where a reducing environment can exist. The reaction rate was found to decrease with a decrease in salinity.

Adsorption kinetics. The results for the adsorption of As(V) on activated alumina, bauxite, and carbon in freshwater and seawater shows the rate of uptake of As(III) by activated alumina and bauxite in freshwater and seawater. In all cases, the adsorption rate is exponential. As(V) was found to be removed from solution much faster by activated alumina than by any other adsorbent. Within the first 10 minutes, in fresh water, 50 percent of As(V) was removed by activated alumina; 40 percent of As(V) by activated bauxite; and 23 percent of As(V) by activated carbon. Rates of As(III) adsorption on activated alumina and bauxite were much slower than those of As(V). As(III) removal was found to increase with time in both freshwater and seawater. The rate of adsorption and extent of arsenic removal decreased with increasing salinity.

pH Effect. The effect of pH on As(V) adsorption by activated alumina, bauxite, and carbon and As(III) adsorption by activated alumina and bauxite was studied in the pH range between 2 and 12. Arsenic (V) is effectively adsorbed in the pH range 4 to 7 by activated alumina and bauxite. As(V) adsorption by activated alumina and bauxite was found to decrease above pH7. Activated carbon adsorbs As(V) better in the acidic pH range between 3 and 5 than in other pH values. Adsorption is sharply decreased at both lower and high pH values. Variations in As(III) adsorption on activated alumina and bauxite over the pH range 4 to 9 were found to be slight. Adsorption decreased sharply above pH 9. These data clearly indicate that activated carbon adsorbs As(V) better in the acidic pH range; yet it exhibits poor adsorption capacity in comparison to activated alumina and bauxite even at pH 4 (the optimum pH for adsorption on carbon).

Effect of solution composition on adsorption. The change in percentage of arsenic removal was found to vary significantly in solutions of different chemical compositions. Arsenic removal is greatly affected by the pH. The percentage of As(III) removal was greatly affected by the initial As(III) concentration. However, As(V) removal was only slightly affected by the initial concentration level.

The adsorption capacities of various absorbents for As(III) and As(V) in solution of various chemical compositions were studied with a residual arsenic concentration of 50 µg/l at equilibrium. The data indicates that the adsorption capacity in freshwater and seawater varied as much as 80 percent in some cases. The adsorption capacity for As(V) on activated alumina was found to vary from 4.11 (freshwater) to 0.81 (seawater) mg As(V) removed per gram of absorbent.

The silica effect on arsenic removal efficiency of various absorbents in freshwater was studied. In general, in comparison with As(V), As(III) removal efficiency was greatly affected by varying amounts of silica. The effect of silica concentrations on the removal of arsenic is not significantly influenced by the matrix background; however, the matrix background does affect the arsenic removal.

It seems that electrostatic interaction and specific adsorption are important mechanisms for arsenic removal by activated alumina and bauxite.

The adsorption study was carried out in solutions of different chemical composition to evaluate the effect of sodium, calcium, chloride and total ionic strength. The rates of adsorption are shown to be slower in seawater than in freshwater. Although rates were reduced with increasing salinity or ionic strength, the adsorption was reduced by no more than 5 percent.

As much as 80 percent reduction in the adsorption capacity of activated alumina in seawater (as opposed to freshwater) conditions was observed. A varying degree of salt effect was observed for As(V) and As(III) adsorption on different adsorbents. In general, As(V) adsorption was affected much more by chemical composition than was As(III).

The data from this study indicates that As(III) is less effectively removed than As(V). Oxidation of arsenite to arsenate is necessary to achieve effective arsenic removal. Oxidation of arsenite to arsenate by chlorine has been used successfully to remove arsenic.

2.4.9 ARSINE GENERATION[2]

Arsine generation processes, while potentially an effective technique for removing certain arsenic forms from wastewater streams, have not found wide acceptance in industry in this application according to the literature search conducted. Presumably, the extreme toxicity or arsine gas and the difficulty in containing a toxic gas when compared to containing a toxic liquid or solid is the primary reason for this. A probable second reason is that arsenic compounds are not always in a form in wastewater streams where the arsine gas can readily be formed. Treatment processes required to obtain predominantly arsenic trioxide in water may not be cost effective when compared to the processes for efficient arsenic removal already discussed.

2.5 EVALUATION OF TREATMENT PROCESSES

Evaluation of arsenic wastewater treatment processes will focus primarily on their applicabilities to Hewlett-Packard's San Jose facility. As has been discussed, HP's facility generates primarily a solid GaAs contaminant with only negligible quantities of soluble arsenic since removal of all soluble arsenic sources at HP would not significantly reduce the hazardous waste quantity generated from their HF Treatment system, no process capable of treating only soluble arsenic can be considered effective.

Table 2.5-1 lists each potential arsenic removal process along with major evaluation criteria with respect to HP's GaAs processing facility. The following discussion will deal with each process individually as opposed to discussing each evaluation criterion individually for all processes.

Liquid-Solid Separation

Filtration[35]

Filtration is an extremely efficient means of separating solid particles from liquid streams. This technique has been in use for many years under almost every type of chemical and physical environment. Figure 2.5-1 lists

TABLE 2.5-1

COMPARISON OF POTENTIAL ARSENIC TREATMENT PROCESSES

Arsenic Removal Process Waste	Form of Arsenic Most Effectively Treated	Possible Applicability to Hewlett Packard	Potential Waste Reduction Efficiency for Hewlett Packard	Operational Characteristics for Hewlett Packard	Potential Health and Safety Concerns	Potential Costs for HP Relative to Other Listed Procedures	Overall Potential Effectiveness in Reducing Hazardous
1. Liquid - Solid Separation							
- Filtration	Solid	Yes	Excellent	Excellent	Low	Lowest	Excellent
- Centrifugation	Solid	Yes	Excellent	Excellent	Low	Lowest	Excellent
- Setting	Solid	Yes	Excellent	Excellent	Low	Lowest	Excellent
2. Precipitation							
- Lime	Soluble	No	Low	Not Applicable	Low	Moderate	Minimal
- Sodium Sulfide	Soluble	No	Low	Not Applicable	Moderate	Moderate	Minimal
- Ferric Hydroxide	Soluble	No	Low	Not Applicable	Low	Moderate	Minimal
3. Coagulation							
- Ferric Sulfate	Soluble	No	Low	Not Applicable	Low	Moderate	Minimal
- Ferric Chloride	Soluble	No	Low	Not Applicable	Low	Moderate	Minimal
4. Solidification	Solid	No	Low	Costly	Low	High	Minimal
5. Adsorption							
- Ion Exchange Resins	Soluble	No	Low	Not Applicable	Low	High	Minimal
- Activated Carbon	Soluble	No	Low	Not Applicable	Low	High	Minimal
- Activated Alumina	Soluble	No	Low	Not Applicable	Low	High	Minimal
- Bauxite	Soluble	No	Low	Not Applicable	Low	High	Minimal
6. Arsine Generation	Soluble	No	Low	Not Applicable	Extreme	High	Minimal

just some of the many types of filters available and their main selection criteria. For most liquid flow streams, filtration efficiency can be designed to what ever level is desired. For Hewlett-Packard, a design efficiency of only 60% or better is required to eliminate HP's solid hazardous waste problem with respect to arsenic. This efficiency is easily attained and, therefore, will be at a relatively low cost. Because of the low temperature and pressure conditions in their wastewater stream, design becomes dependent on the particle distribution of the solids present. As this study has been completed, successful installation of effective filtration equipment is a matter of routine chemical engineering practice [32].

Operational characteristics of the required filtration equipment like other liquid-solid separation processes would be rather simple and would offer excellent reliability with full automatic operation possible. This hands-off operation would reduce health and safety concerns to an absolute minimum.

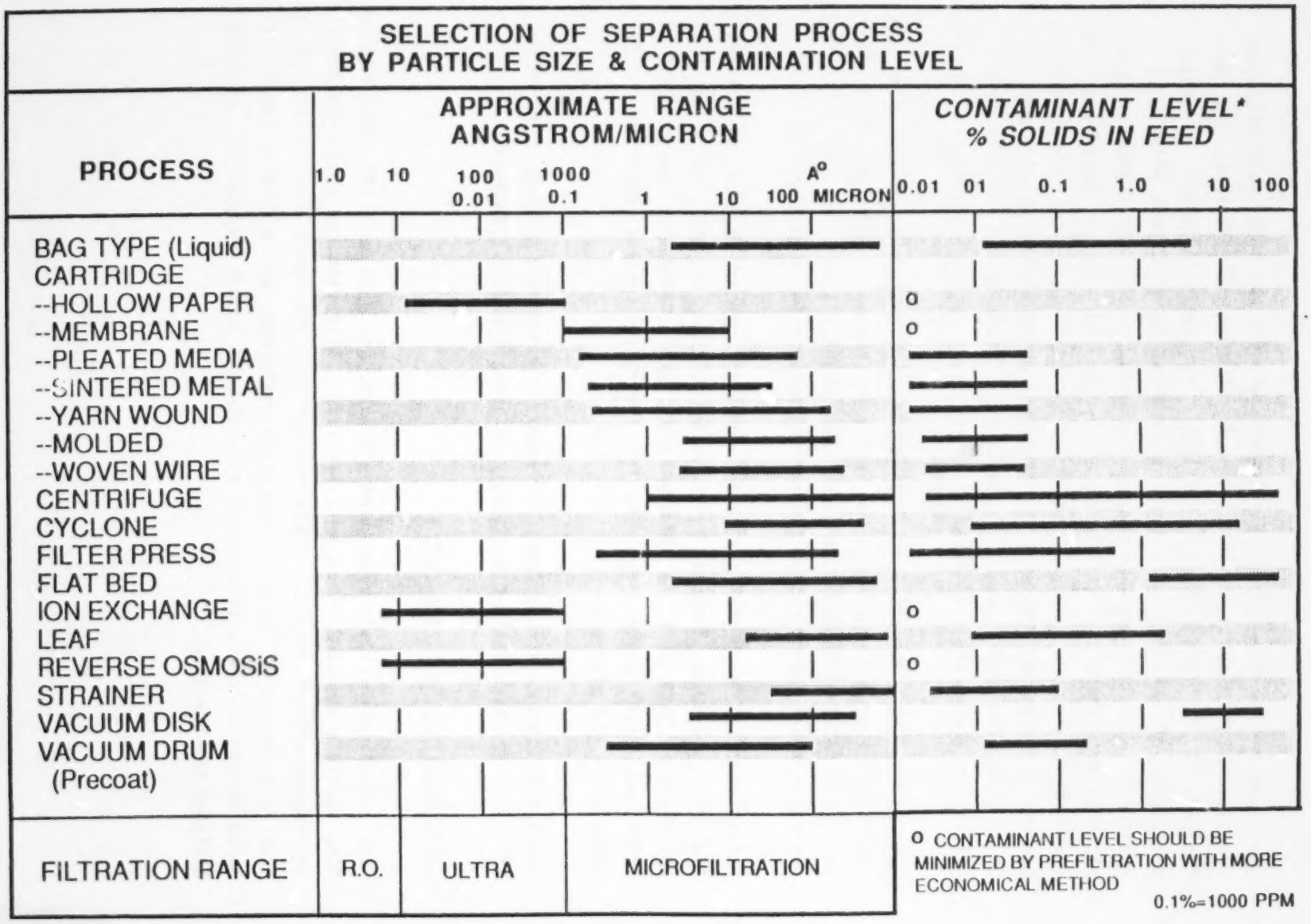
Potential costs to HP for filtration equipment should be among the lowest of treatment processes because of high efficiency, minimal operating and maintenance costs (i.e. no chemical addition or residence time constraints), total automation capability, and the favorable ambient conditions (low temperature and pressure) for filtration.[32]

Overall potential effectiveness in reducing arsenic-laden hazardous wastes at HP's facility is excellent and should be among the most effective.

Centrifugation and Sedimentation

These other solid-liquid separation processes are also very effective and could find possible application at HP's facility. They both share all the positive attributes with filtration. Selection of this equipment over filtration is usually a matter of personal operating preference and available space. All three processes could be equally effective in solids removal if properly designed and operated.[32]

FIGURE 2.5-1


SELECTION OF SEPARATION PROCESS
BY PARTICLE SIZE & CONTAMINATION LEVEL
PROCESS
APPROXIMATE RANGE
ANGSTROM/MICRON
1.0
10
100
1000
0.01
0.1
1
10
100
A°
MICRON
CONTAMINANT LEVEL*
% SOLIDS IN FEED
0.01
01
0.1
1.0
10
100
BAG TYPE (Liquid)
CARTRIDGE
--HOLLOW PAPER
--MEMBRANE
--PLEATED MEDIA
--SINTERED METAL
--YARN WOUND
--MOLDED
--WOVEN WIRE
CENTRIFUGE
CYCLONE
FILTER PRESS
FLAT BED
ION EXCHANGE
LEAF
REVERSE OSMOSIS
STRAINER
VACUUM DISK
VACUUM DRUM
(Precoat)
o
o
o
FILTRATION RANGE
R.O.
ULTRA
MICROFILTRATION
o CONTAMINANT LEVEL SHOULD BE MINIMIZED BY PREFILTRATION WITH MORE ECONOMICAL METHOD
0.1%=1000 PPM

Precipitation

Effective arsenic removal can be achieved with these processes if the arsenic form were soluble. Should removal of arsenic from the cleaning and etching wastestreams become desired, this process, like most of the others discussed below, would be very effective.[32] Because this stream now contributes only a negligible portion of the arsenic to the HF Treatment sludge cake, installation of such equipment would not be expected.

Precipitation processes would be necessarily more expensive than any liquid-solid separation system because precipitation chemicals must be added followed by some liquid-solid separation process. Therefore, it is logical to assume that all systems converting soluble arsenic to some insoluble compound and then reducing that insoluble compound in volume by some means will be more costly to install and operate that most systems requiring only recovery of insoluble arsenic.[33,9,26]

Because of the above conclusions, precipitation would not appear to be applicable to HP's facility.

Coagulation

These processes are very effective in removing soluble arsenic by addition of such chemicals as ferric sulfate or ferric chloride[11]. As with the above mentioned precipitation processes, a means of liquid-solid separation is necessary in conjunction with coagulation techniques. In addition, pH adjustment to an alkaline point is usually necessary and would, therefore, add additional operating chemical costs.[11]

Coagulation processes would appear to have little utility in removal of insoluble arsenic and is not considered viable for HP's San Jose facility on that basis.

Solidification

This process removes the solvent (water in the case of HP's wastewater stream) and mixes the remaining solids and precipitated salts with such binders as asphalt or thermoplastic materials. The energy requirements for water evaporation would be very high. Additionally, this process would create additional hazardous waste because of the waste concentration in a large weight of binder. This process is more ideally suited to recovery of radioactive solids and encasement in a volume of inert binder prior to long-term disposal.[27]

Adsorption

These arsenic removal processes are rated the highest in their efficiency with respect to soluble arsenic (and many other ions). If they were used in a wastewater stream with solids present as is the case for HP, it would act as a filter and is, therefore, not suited for this purpose. Adsorption is commonly used to treat low-levels of soluble heavy metal compounds in wastewaters of many industries. The processes proven reliability and efficiency are discussed throughout the literature [17,19,28,27,33].

Arsine Generation

Since arsine generation requires the reactant to be arsenic trioxide in a soluble form prior to generating arsine gas, any costs or processes necessary to convert arsenic compounds to this form would be included in this process. For HP, this would be extremely costly in terms of equipment, chemical additives, energy costs (for acidic conversion to arsenic trioxide) and for gas containment systems. Because HP stresses safety above other process constraints, this type of process would meet with serious obstacles. Therefore, its application for arsenic removal would very limited.

2.6 ENVIRONMENTAL PERSPECTIVE

INTRODUCTION

Portions of the following discussion address the health aspects of arsenic. Many of the parameters do not pertain to gallium arsenide (GaAs) unless the arsenic in GaAs is converted to free arsenic. In particular, GaAs is much less toxic than free arsenic.[24]

Arsenic, may present a health hazard to humans when it is released into the environment as a consequence of an industrial process. The preponderance of clinical and epidemiological evidence regarding the effects of arsenic pertains to trivalent inorganic arsenic. Much of this evidence suggests that trivalent inorganic arsenic is a carcinogen. Some limited evidence suggests that pentavalent inorganic arsenic may also be carcinogenic.

The primary routes by which arsenic enters the human body are inhalation and ingestion. Both trivalent and pentavalent arsenic are mutagenic and teratogenic in animal tests. Animal toxicity studies indicate that trivalent arsenic is several times more toxic than pentavalent arsenic.

Epidemiological studies of smelter workers show excess lung cancer risk in individuals exposed to arsenic trioxide, and several studies indicate that the risk increases with increasing duration and level of exposure. The currently available experimental and epidemiological evidence does not provide an adequate basis for gauging the effects of chronic low-level exposure to arsenic compounds. It is reasonable to assume that smaller dosages of inhaled arsenic could be involved with the development of cancer, since inhalation is a more efficient route of entry to the body than ingestion.

It is difficult to determine a specific level of exposure associated with a specific level of risk because the precision of ambient air measurements is low; the level may be incorrect by as much as one order of magnitude. American Conference of Government-Industrial Hygienists Inc.[4] has determined a threshold limit (TLV) of 0.2 mg per cubic meter of air.

California Regulations for Managing Hazardous/Special/Designated/ Non-Hazardous Wastes

California Administrative Code Title 8, Chapter 4, Subchapter 7:

The general industry safety codes (Appendix B) specifies a Permissible Exposure Limit (PEL) of 10 micrograms per cubic meter of air determined as an average over an 8-hour period. Also, no employee may be exposed to any skin or eye contact with arsenic trichloride as skin or eye contact is likely to cause skin or eye irritation.

The regulatory requirements of employer responsibility, implementation of health and safety measures, work practices, worker protection plan, housekeeping, signs and labels, employee training program, employee medical examination plan, air monitoring and measurement procedures are detailed in Appendix B.

California Administrative Code Title 22, Chapter 30:

These regulations deal with management of hazardous and extremely hazardous waste. The sections which apply to managing arsenic waste are as follows.

Section 66680.

This list of chemical names and common names includes arsenic compounds as having potential extremely hazardous properties.

Section 66699.

This section entitled Persistance and Bioaccumulative Toxic Substance, sets limits of Soluble Threshold Limit Concentration (STLC) and Total Threshold Limit Concentrations (TTLC) for chemicals. Arsenic and arsenic compounds are included on the list. The TTLC and STLC values for arsenic and/or arsenic compounds as set in this section are:

STLC	5 mg/l
TTLC	500 mg/kg

If the concentrations are less than the TTLC and STLC, limit approvals should be obtained from the Department of Health Services to exempt the waste from management as hazardous waste.

Section 66472.

This section states that all generators of hazardous wastes must obtain an EPA identification number and the wastes should not be offered for transportation or to treatment, storage, or disposal facilities without obtaining an EPA identification number.

Section 66508.

This section states that a generator can accumulate hazardous waste for 90 days or less without a permit. If a generator plans to store these wastes for more than 90 days, a facility permit has to be obtained unless the Department of Health Services has granted an extension to the 90 day period.

Section 66723.

Total Threshold Limit-Concentration Values for Persistant and Bioaccumulative Toxic Substances in Extremely Hazardous Waste are listed in this section. The TTLC limit - as set in this section for arsenic and/or arsenic compounds is 50,000 mg/kg as As.

Section 66900.

This section lists chemicals names and their concentrations regarded as hazardous wastes or restricted hazardous wastes. Liquid wastes containing chemicals listed in this section at concentrations greater than the specified limits are restricted from land disposal. Arsenic and/or arsenic compounds are included on the list. The limit set in this section for arsenic and for arsenic compounds is 500 mg/L.

Section 66905.

Land disposal restrictions and schedule for all the chemicals listed in Section 66900 and restricted concentrations are set here. This section also fixes the commencement date for restrictions on land disposal. For arsenic and/or arsenic compounds, land disposal restriction commenced on January 1, 1984.

Section 66305.

This section fixes the responsibility on the generator to determine if the waste is classified as hazardous or non-hazardous.

Section 66471.

Hazardous Waste Determination Requirements for Waste Generators are furnished as guidelines to determine if the waste is hazardous or non-hazardous.

Section 66744.

This section informs the generator of hazardous waste to obtain prior written approval from the Department of Health Services for any waste to be classified as a special waste.

Section 66310.

This section stipulates conditions under which the Department of Health Services can grant a variance from the requirements of hazardous waste management.

California Administrative Code Title 23, Subchapter 15, Discharge of Waste to Land:

The sections which apply to disposing of arsenic waste are detailed below. The Regional Water Quality Control Board (RWQCB) has to approve any waste disposal for which the Department of Health Services has issued a variance. The RWQCB has its own standards for classification of wastes. Figure 2.6-1 explains the various classifications, and Figure 2.6-2 explains the criteria adopted for the different classifications.[30] The classifications of RWQCB are in reference to the increased hazard or water quality threat posed by the wastes.

Section 2521.

This section defines the type of wastes that can be treated as hazardous waste and states that such waste should be disposed in a Class I Waste Management Unit.

Section 2522.

This section defines the type of wastes that can be treated as designated wastes and states that such wastes should be discharged in Waste Management Units Class I and Class II if approved by RWQCB for such disposal.

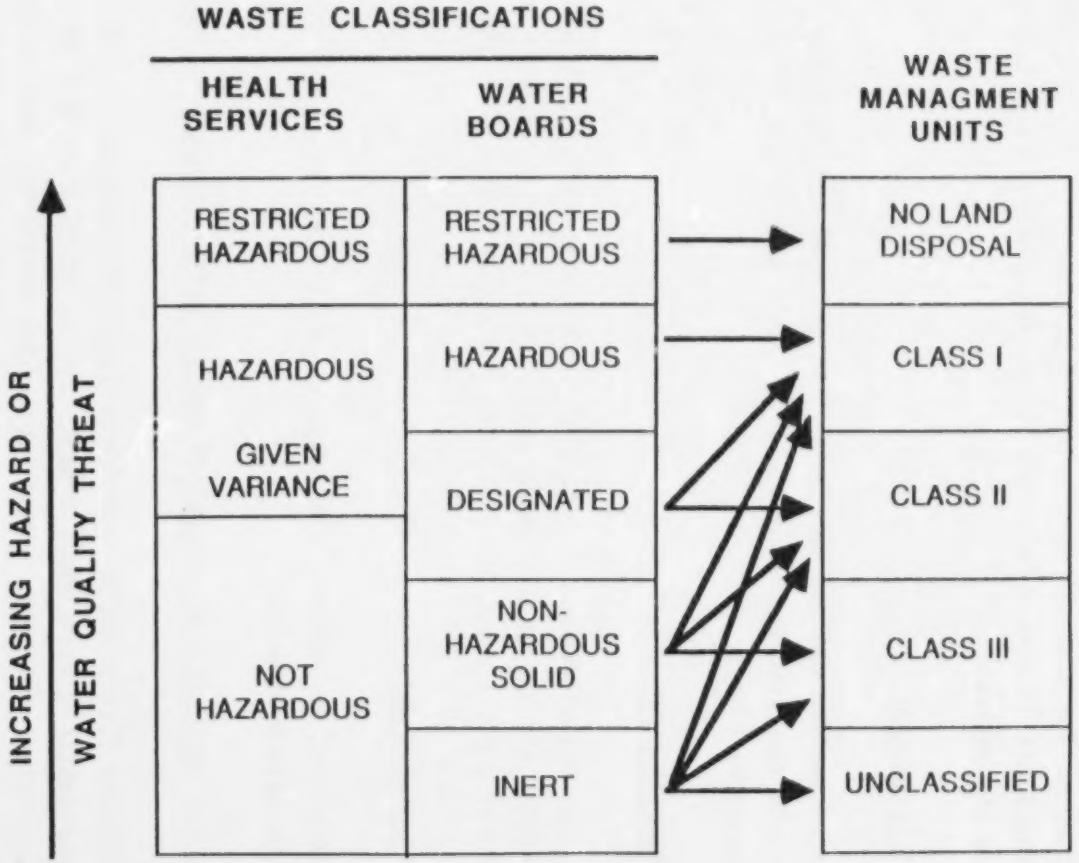
Section 2523.

This section defines the type of waste that can be classified as non-hazardous wastes.

2.6.1 REDUCTION OF VOLUMES OF ARSENIC WASTE GENERATED STATEWIDE

Because filtration is a physical separation process, its application to any wastewater stream where arsenic is in solid form can be considered possible. Only when a detailed process wastewater chemical characterization has been completed as has been done for HP's San Jose facility, can an evaluation be begun of which arsenic removal process is best.

FIGURE 2.6-1
WASTE AND UNIT CLASSIFICATIONS USED IN CALIFORNIA



(SOURCE: REFERENCE 2)

If the arsenic-laden hazardous waste generated in HP's HF Treatment System (treatment of hydrofluoric acid) is a common method of treatment for other GaAs microchip manufacturer's process wastewater, then it could be projected that filtration of solid GaAs would greatly reduce this type of waste throughout the state.

2.6.2 ACCEPTABILITY BY INDUSTRY

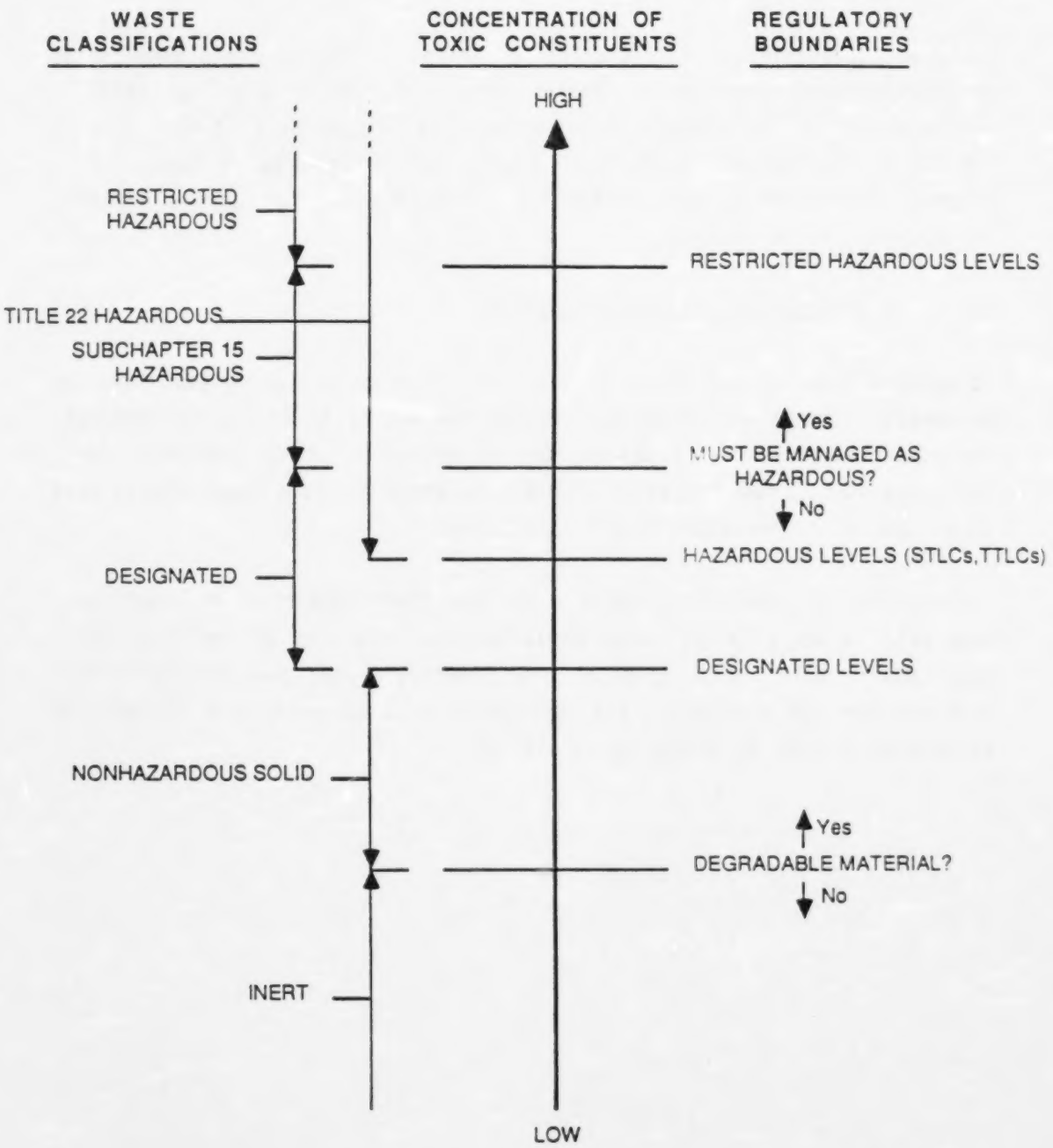
Although acceptability of filtration for arsenic wastewater treatment cannot be directly assessed without chemical characterization data from other manufacturers in the microelectronics industry, it can be said that if such arsenic wastewater has substantial amounts of solid arsenic compounds present, filtration usually presents the most economic and simple process for such wastewater cleanup.

2.6.3 TRANSFERABILITY TO OTHER INDUSTRIES

It appears that the transferability of filtration as a cleanup technique for wastewater streams with hazardous solids present is as easily carried out for other industries as it can be for the microelectronics industry. This technique is not new for solid-liquid separation and is already widely used in all manner of processes in all industries.

Transferability, therefore, depends on the identified need for such a separation process be it based on an economic basis or an environmental one. Again, only when a chemical characterization has been completed for each manufacturer's facility can application of filtration as a liquid/solid separation process be prudently considered.

FIGURE 2.6-2
RELATIONSHIP BETWEEN WASTE CLASSIFICATION AND CONCENTRATIONS OF TOXIC CONSTITUENTS



REFERENCES

1. Sisler, et al. 1963. College chemistry - A systematic approach. Second edition. Published by Macmillan Company, New York.

2. Cotton, F.A. and G. Wilkinson. 1966 Advanced Inorganic Chemistry Second edition. Published by Interscience Publishers, New York.

3. Frey, P.R. 1961. College Chemistry - Second Edition. Published by Prentice Hall Englewood Cliffs, New Jersey.

4. 1980 Document of the Threshold Limit Values Fourth Edition. Published American Conference by Governmental Industry Hygienist, Inc., Cincinnati, Ohio.

5. Cherinksi, S. N. and F. I. Ginzburg, Purification of arsenious waste waters, 1970. Water Pollution Abstract, 14:315-316, 1941.

6. Anonymous. 1970 The economics of clean water, Vol. III, Inorganic Chemicals Industry Profile, U. S. Dept. of Interior, Washington, D.C.

7. Swain, R. E. 1939 waste problems in the nonferrous smelting industry, Industrial Engineering Chemistry, 31:1358-1361, 1939.

8. Stooff, H. and L. W. Haase. 1938 Occurrence and removal of arsenic in drinking waters. Chemical Abstract, 32:6370 (4).

9. Nelles, R. A. and F. D. Amato, 1950 Treatment of arsenical waters with lime. Water Pollution Abstract, 23:125, 1950.

10. Viniegra, G. and R. E. Marquez. 1965 Chronic arsenic poisoning in the Lake Region: Section 4. Treatment of Drinking Water. Water Pollution Abstract, 38:430-431, 1965.

11. Shen, Y. S. and C. S. Chen. 1964. Relation between black-foot disease and the pollution of drinking water by arsenic in Taiwan. In Proceedings from the Second International Conference Water Pollution Research, Tokyo, 1-173-190, Pergamon Press, New York.

12. Bellock, E. 1972. Arsenic Removal from Potable Water. Journal American Water Works Association, 63:454-458.

13. Curry, N. A. 1972. Philosophy and methodology of metallic waste treatment, presented at 27th Purdue Industrial Waste Conference, Purdue University.

14. Maruyama, T., S. A. Hannah and J. M Cohen. 1972. Removal of heavy metals by physical and chemical treatment processes. Presented at 45th Annual Conference, Water Pollution Control Federation, Atlanta, Georgia.

15. Electrolytic Metal Corp. 1960. Recovery of Manganese from Solutions Containing Iron, Manganese, Nickel, and Cobalt - Patent, Chemical Abstract, 54:12960 (c).

16. Magnusen, L. M., T. C. Waugh, O. K. Galle and J. Bredfeldt. 1970. Arsenic in detergents: Possible danger and pollution hazard. Science 168:389-390.

17. Sigworth, E. A. and S. B. Smith. 1972. Adsorption of Inorganic Compounds by Activated Carbon, Journal American Water Works Association, 64:386-391.

18. Buswell, A. M., R. C. Gore, H. E. Hudson, H. C. Wiese, and T. E. Larson. 1943. War problems in analysis and treatment, Journal American Water Works Association, 35:1303-1311.

19. Berezman, R. I. 1965. Removal of inorganic arsenic from drinking water under field conditions. Water Pollution Abstract, 29:185.

20. Nilsson, R. 1971. Removal of metals by chemical treatment of municipal waste water. Water Research, 5:51-60.

21. Dorr-Oliver, Inc. 1968. Cost of waste water treatment processes, Robert A. Taft Water Research Center Report, No. TWRC-6, U. S. Department of Interior, Washington. D.C.

22. Lund, H. F. 1971. Industrial Pollution Control Handbook. McGraw Hill Book Co., New York.

23. Sotoharu Goto. Filter for removal of heavy metals. Translated from Japanese Kokai Patent Publication No. Sho 56-53741 91981).

24. U. S. Department of Commerce. 1984. National Technical Information Source. Health Assessment Document for Inorganic Arsenic Final Report. PB84-190891.

25. Bhattacharyya, D. et al. 1981. Precipitation of heavy metals with Sodium Sulfide: bench-scale and full-scale experimental results. AIChE Symposium Service, 7209 V.77 Water.

26. Doyle, Richard D. 1979. Use of an extruder evaporator to stabilize and solidify hazardous wastes. Proceedings Mid Atlantic Industrial Waste Conference Pennsylvania, pp. 56-62.

27. Huang, C. P. and P. L. K. Fu. 1984. Treatment of arsenic (V) containing water by the activated carbon process. Journal Water Pollution Control Federation, V. 56, pl-1, N3, pp. 233-242.

28. Gupta, K. S. and K. Y. Chen. 1978. Arsenic removal by adsorption. Journal Water Pollution Control Federations, March, pp. 493-505.

29. Clifford, D. 1982. Processes for removal or inorganic contaminants from water. Water Engineering and Management Reference Handbook, pp. 31-38.

30. Marshack, J. B. 1985. Waste classification and cleanup level determination guidance document. California Regional Water Quality Control Board, Central Valley Region.

31. Perlmutter, B. A. 1983. Principles of Filtration. Technical Brochure, Pall Well Technology Corporation, WER 5300, February.

32. Perry, R. H. Third Editions, Chemical Engineers Handbook, McGraw-Hill, 1973, Sections 16 and 17.

33. Wade, R. et. al. 1981. Semiconductor Industry Study. State of California Department of Industrial Relations, Division of Occupational Safety and Health.

34. Skripach, T. et. al. 1971. Removal of Fluorine and Arsenic from Wastewater of the Rare Earth Industry. Proceeding 5th International Conference Water Pollution Research 2:III-34.

35. Anonymous. 1986. Filtration and Separation, Special Advertising Section, Chemical Engineering, October 27.

LIST OF INVENTIONS REPORTED AND PUBLICATIONS

Envirosphere and Hewlett-Packard companies in cooperation with the Department's Alternative Technology and Policy Development Section plan one or more scientific publications and/or conference presentations as a result of this project.